

N. F. LASHKO, S. V. LASHKO-AVAKYAN

BRAZING and SOLDERING of METALS

Translated from Russian

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N. F. Lashko, S. V. Lashko-Avakyan

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Translation of the Russian book:

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PAIKA METALLOV

Mashgiz

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The present book provides basic information on the physical and chemical processes and structural transformations taking place during soldering* of metal, as well as on the design of soldering joints, the preliminary treatment of the parts to be joined, solders (soldering alloys) and fluxes, the technology and methods of manual and mechanized soldering, and finally on soldering of various base metals and their alloys.

This is a handbook for researchers and engineers who are engaged in designing and applying the soldering process in various fields of engineering.

L. S. MARTENS, EDITOR

Editorial Office for Heavy Mechanical Industry
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* [Since the term "paika" covers both brazing (hard soldering) and soft soldering, the term soldering is used throughout by the translator and, unless otherwise defined, refers to both processes. In this connection the reader's attention is called to the introduction].

FOREWORD

Soldering of metals and alloys, together with furnace welding, represents one of the oldest methods of securing a permanent joint between different parts. In order to distinguish fusion welding from other welding methods devised at the end of the last century, this method has been termed "soldering" by N. N. Benardos. Some basic principles of soldering laid down in ancient times and still applied today, proved to be insufficient for securing many kinds of permanent joints required for modern machinery building.

Despite the tremendous number of patent rights granted in various countries, these, in their majority, remained unused, or else experience in their use was not published till recently.

Soldering of metals covers a great number of closely related fields: physics and chemistry of the interaction of gaseous and liquid fluxes with oxides and other substances which are formed on the surface of the metal parts to be soldered; metallurgy of solders, of the soldered seam and of the zone of thermal influence in the joined area; design and mechanical properties of soldered joints; technology of soldering, etc. These questions, as E. Lüder duly pointed out in his manual "Handbuch der Löttechnik", cannot be covered by a single person.

The intention of the authors of the present study has been to present known data on soldering processes in the light of their own experience as well as in the light of the general knowledge of the physical and chemical processes of soldering. The authors do not pretend to have given an exhaustive treatment of all the problems involved and admit that many of them still remain questionable.

The first section of the book deals with the distinguishing features of the design of soldered joints. Some problems concerning the interaction of liquid solders with the parts to be soldered, their crystallization and internal structure of the soldered seam and its influence on the quality of the resulting connections are treated in the second section. Characteristic features of crystallization occurring in the soldered seam, as well as of the internal structure of the latter have been published earlier in the authors study, "Physical Metallurgy of Welding".* In the third section, problems are examined connected with the selection of solders and fluxes required. The fourth section deals with the basic methods of soldering, which are determined by the methods of heating the parts to be soldered and of removal of scale and oxide films, as well as by the methods of preparing solders. In the fifth and last section essential features of soldering various alloys to different kinds of base metal are described.

INTRODUCTION

Soldering of metals is a variant of the welding process /1/. Like other welding methods, soldering can be used for assuring a permanent joint between the parts and for surfacing metallic parts. The process of surfacing metallic parts by means of a solder is termed tinning. Tinning may be an independent process as in zinc plating, aluminum coating, etc, or it may be a preparatory operation prior to the final and permanent joining of the parts involved.

The following characteristic features distinguish soldering from other welding methods:

1. Joining of metallic parts by soldering is achieved by the melting and crystallization of the metal filler, either introduced between the adjoining faces or spontaneously formed while these are heated.

In many cases of soldering, it is not necessary to have a special metal or alloy inserted between the faces of the parts to be soldered. There are some processes where soldering may be done even without using solders.

* [Metallovedenie svarki].

Any metal alloy forming a eutectic or a continuous row of solid solutions with a minimum melting point can be soldered without any solder (the so-called reaction-soldering process), by simply heating it to a minimum melting temperature, lower than the melting point of the parts to be joined. Therefore, the degree of distortion and oxidation of the metallic parts in soldering is smaller than in welding. Most commonly used are soldering methods in which a special solder is inserted between the surface of the parts to be united.

2. The filler metal (in this particular case the solder) differs in its composition and properties from the base metal of the joined parts. Its melting point must be lower than that of the base metals or alloys. Unlike welded parts, metallic pieces soldered with a low-melting solder can be separated and then resoldered after their rearrangement or replacement by other parts.

During soldering the metallic parts to be joined may partially undergo a surface melting, as a result not of their heating but of a chemical reaction (development of the eutectic and changes in composition which are due to the diffusion processes during soldering, and which cause a lowering of the melting point of the metals or alloys to be soldered).

3. The filling of the space (gap) between the adjoining surfaces with the filler metal is partially due to the action of capillary forces. In braze welding, a special case of welding, this action is insignificant.

On the strength of the above-mentioned peculiarities which are characteristic and sufficient for a definition, the soldering process may be defined as follows. Soldering is a process of assuring a permanent joint, or building up a surface on metallic parts, by means of a metallic filler, the solder, introduced in a liquid state between the surfaces to be joined or becoming liquefied during its heating below the melting point of the base metal or alloy. Due to the action of capillary forces the liquid filler metal fills the gap between the faces of the parts to be joined.

This definition of the soldering process is very different from other definitions; for instance it does not imply the use of a solder. The given definition is purely technological; it generally links the basic operations in making a soldered joint, with such processes of surface treatment of the adjoining parts as coating of metallic parts, by dipping them in baths of melted metals or alloys. Sometimes these operations are required to increase the resistance against corrosion or oxidation or to improve other properties of the joined parts.

Some difficulties may arise also in the definition of the type of joining between two metals or alloys having different melting points. If a joint is a result of fusing the lower melting metal without melting the other metal (e.g. joining of aluminum to steel or copper having aluminum impurities), such a process includes the characteristic features of both soldering and welding. The characteristic features of welding are prevalent, if joining is made without intervention of capillary forces. This special process of joining can also be termed braze welding. Braze welding is a process whereby the base metal is not melted, joining being made by methods characteristic of a welding process without intervention of capillary forces.

Although the soldering methods are usually divided into two types: "soft" soldering and "hard" soldering (brazing), their characteristic features are not sharply defined: the temperature delimitation between the "soft" and "hard" soldering process was changed repeatedly.

Most of the authors in using the term "soft" and "hard" soldering are applying the term "hard soldering" to the soldering of metals and alloys with solders having a melting point higher than 600° C (solders on silver, copper, nickel or other bases).

On the other hand it is customary to term "soft soldering" such processes which use solders of fusible alloys (on an indium, antimony, tin, cadmium, lead or zinc base). A temperature of 450° C is usually accepted in numerous studies on soldering as an upper limit of the melting temperature of soft solders. For instance, in England [and USA] the term "brazing" is used to denote the "hard" soldering process, whereas the term soldering is used only for "soft" soldering. Such a classification of the soldering processes makes it more difficult to define joining methods which use solders on an aluminum base, the melting point of which ranges from 450° to 600° C. In accordance with the definition given by the International Welding Institute, "soft" soldering applies to processes where solders with a melting point below 450° C are used, whereas "hard" soldering refers to solders having a melting point above this value. This is an arbitrary definition since zinc-base alloys of the system Zn-Cu-Al, which are used or may be used for soldering purposes, have a melting point above this limit, although they are classed as "soft" solders.

E. Lüder's proposal to define the notions of hard and soft solders in accordance with their basic alloys (heavy or light alloys) /3/ increases only the confusion in the classification of the various methods of soldering. According to the existing practice Lüder suggests that we term "soft" the soldering of heavy alloys, when the parts are joined with solders having a melting point below 450° C and to term "hard" the soldering of parts with solders which have a melting point above 600° C. As asserted by Lüder, hard soldering of light alloys is a process of joining metallic parts by means of solders containing more than 70 per cent light metals, whereas soft soldering is a process of joining with solders having more than 50 per cent heavy metal content.

Owing to this state of confusion in the definition of the term "soft" and "hard" soldering, the term soldering only is used throughout this book. It would be reasonable to subdivide soldering into groups of base metals of the soldering alloys used. Soldering with low-melting metal-base solders (In, Pb, Sn, Cd, Zn) could be called soldering with low melting solders, without limiting, however, the upper melting temperature of the soldering alloy.

According to the methods of preparing, introduction, and action of the soldering alloy, we may distinguish between conventional and reaction soldering. In the first method of soldering, the solder is fed in a liquid state into the space between the adjacent surfaces without changing its chemical composition throughout the melting process. The reaction soldering process is based on the fact that the filler metal between the adjoining surfaces is formed as a result of physical and chemical processes occurring while soldering. An essential feature of metal soldering is the metallic bond between the base metal and its metallic filler which ensures a rigid and durable joint. For setting up a metallic bond, the diffusion processes are of great importance from the author's standpoint, since without these processes no durable connection of metals and alloys can be accomplished.

According to some researchers, during soldering of many metals (particularly aluminum) with low-melting alloys, there is no interdiffusion

between the solder and the base metal, i.e. there is no cohesion between them but only adhesion /4/. It is well known that reliable joining of aluminum with low melting solders may be done only at a temperature above 250° C when the rate of diffusion attains a high value. Soldering of aluminum and its alloys at temperatures below 250°C cannot secure connections with a rigid and durable bond between the metallic parts.

Of special technological importance is soldering of metals on materials such as glass and ceramics. Since the bond on such oxides is non-metallic, the adhesion of metals to oxides differs from metal to metal /5/. The process of soldering oxides to oxides by solders also formed of oxides, is associated with a chemical reaction characteristic of ionic compounds.

At present, soldering is widely used in various branches of industry. In machine building, soldering helps in repair and maintenance work as well as in manufacturing of blades and rotors for turbines and jet engines, in joining of pipe lines, automobile parts, hollow steel blades, radiators, cylinder ribs for air-cooling, bicycle frames, industrial vessels, different cellular materials, compound instruments and tools, gas producing and handling equipment, die-fittings, etc.

In the electrical industry and the construction of tools and devices soldering is often the exclusive method for joining metallic parts; e.g., for manufacturing of: wave-guides, electrical lamps and radio valves, television sets, different units and setups, parts of electrical equipment (collars, lugs, etc), vacuum and electrovacuum devices; soldering is also used in assembling electrical and radio-outfits, for fusibles, etc; apart from this it has a growing use in joining connection bars (bus bars), conductors etc.

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* [In the bibliographic references included in this book translations of titles of periodicals and of names of publishers are given in parentheses, while titles of articles in periodicals are given in translation only. When requesting a publication from a library, specify—for books—author and transliterated title, and—for periodicals—author and the numbers given in the reference (volume, number, pages, etc), since the publications are so recorded in Library catalogues.]

Section One

DESIGNING OF SOLDERED JOINTS

Chapter I

TYPES OF SOLDERED JOINTS

§ 1. Basic Types of Soldered Joints

The design of soldered joints depends on the physical and chemical processes involved as well as on the properties of the soldered joint. Designing of soldered joints has its peculiarities as compared with other types of joints (welded, riveted, adhesive-bond joints, etc).

A soldered seam is formed by the capillary attraction when the space between the adjoining surfaces is being filled with molten solder. In some cases the action of gravity can be added to the capillary action.

The quality of a soldered joint is mainly determined by the compactness of the filling with molten solder as well as by the strength of bond between the solder and the base metal.

By capillary soldering only a limited number of types of joints can be obtained which constitute the basic elements of practically possible joint. The types of soldered joints depend on the position of the parts to be soldered, so as in butt joints, corner or tee joints, crossed and edge or lap joints.

Parallel parts may be placed one behind the other or one above the other. In the first case the soldered face may be perpendicular to the basic part or at a certain angle (butt joint or scarf joint) to it.

When overlapping the parts to be joined, the soldered face is parallel to the surface of the parts to be joined.

Crossed (intersectioned) parts may have a tee joint or a corner joint. The soldered face may be placed at a certain angle to the face of the base parts or parallel to one of the parts and perpendicular to the others.

Superposed parts may be soldered along a continuous line of contact or at some points (spots) only.

In all these types of soldered joints the soldered face may be flat or curved.

Thus, the basic types of soldered joints are the butt joint, the lap joint and the scarf joint. All the other types are merely a combination of these fundamental joints. In Figure 1 a schematic representation of the basic types of soldered joints is given.

These types of joints may also be used in other methods of joining (welding and riveting).

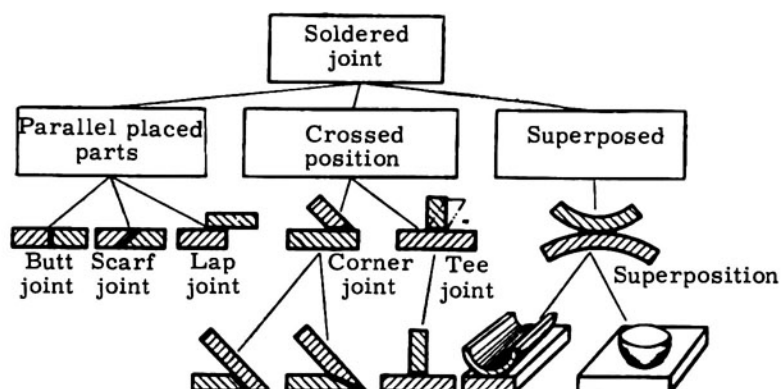


Figure 1. Basic types of soldered joints

§ 2. Designing Features of Butt, Scarf and Lap Joining of Parallel-Placed Parts

Among the soldered joints of parallel parts, the lap-type joint has found a particularly wide use. A soldered connection having a mechanical strength equal to that of the basic part may be obtained mainly through a lap joint which permits us to utilize all the advantages of the soldering process. In a high quality soldering process the solder fills completely the space between the faces to be lap-joined, thus eliminating spreading of flux which otherwise would reduce the mechanical strength of the part by subjecting the soldered joint to corrosion; therefore, the basic type of soldering is the lap joint /1/-/5/.

The soldered seam of a butt joint is less rigid than the basic metal. Failure of soldered butt joints occurs mainly along the soldered seam. Despite the lesser rigidity of the butt joint it may be applied in works requiring less accuracy or to parts not subjected to heavy loads, e.g. in joining fittings to pipe-lines, in connecting ends of copper wire followed by its cleaning and drawing to a smaller diameter, in manufacturing parts if their cutting from a whole piece of metal is inconvenient etc.

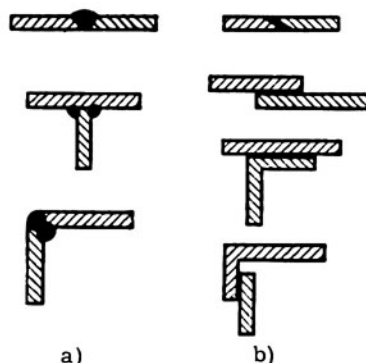


Figure 2. Design features of some types of (a) soldered and (b) welded joints

Due to the larger area of the soldered faces, the scarf joint has a greater mechanical strength than the butt joint but some difficulties of its technique reduce the field of its application. Scarf joints are mainly used when a given size of the joint has to be maintained after the soldering process (e.g. in soldering lead pipes).

Butt joints are not suitable for parts to be bent or stamped during their manufacturing or for parts subjected to heavy static loads, to shocks and vibrations.

It must be emphasized that, unlike soldering, in a welding process butt joints have a greater strength and a better technique than other types of joints, therefore preference is given to them in most of the welding operations.

In designing soldered joints, it is not practical to adopt the structural elements directly from the welding practice. For comparison, in Figure 2 some soldered and welded types of joints are given.

The above mentioned types of joints can be made by soldering parts with a flat or curved soldered face.

Soldered joints with a circular seam are called tubular joints; soldered joints with a flat face of the joint are called flat joints.

Flat soldered joints. Flat soldered joints are not so frequent as tubular joints, being mainly used for manufacturing boxes and parts of different devices, for soldering tools, instruments, contacts, tubular fittings of rectangular cross-section, etc. The lap joint is the basic type of this kind of connection.

The strength of flat lap joints depends on the area of the soldered face, i.e. on the area of the overlapped section. Such types of joints can be achieved in different kinds, according to the design and purpose of the finished product. In Figure 3 some types of flat soldered joints are represented. The butt joint 1 has the smallest mechanical strength; the other types of soldered joints (2-10) are stronger, mainly owing to the increased area of the soldered face as a result of combining the lap and butt type of joint.

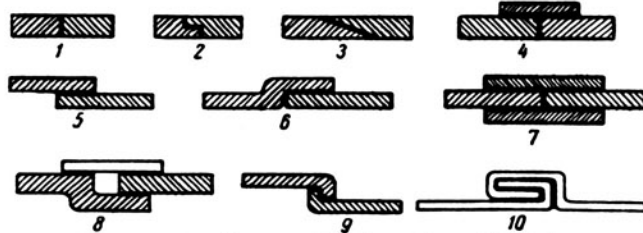


Figure 3. Types of flat soldered joints

Scarf soldered joints should be applied in joining sheets, above 1 mm in thickness as well as for soldering side-walls to detachable bottoms (lids) of thin-walled vessels. In the following the length of the lap section (lap) is given according to the thickness of the sheet to be soldered:

Sheet thickness, mm	1—1.5	2—3	3.5—5	5—8	8.5—13
"Lap" thickness, mm	10	15	20	25	30

Locating of soldered seams on places with a greater concentration of stresses should be avoided and their reinforcing by the adjacent parts be assured. Figure 4 shows correct and incorrect designs of soldered parts subjected to breaking strains, shocks and vibrations [6].

Tubular soldered joints. This type of joint is most commonly used, for instance in flange connections, in joining sockets to tubes or rods,

in connecting blind flanges to pipes, in soldering elbows, expansion loops, closed vessels, etc.

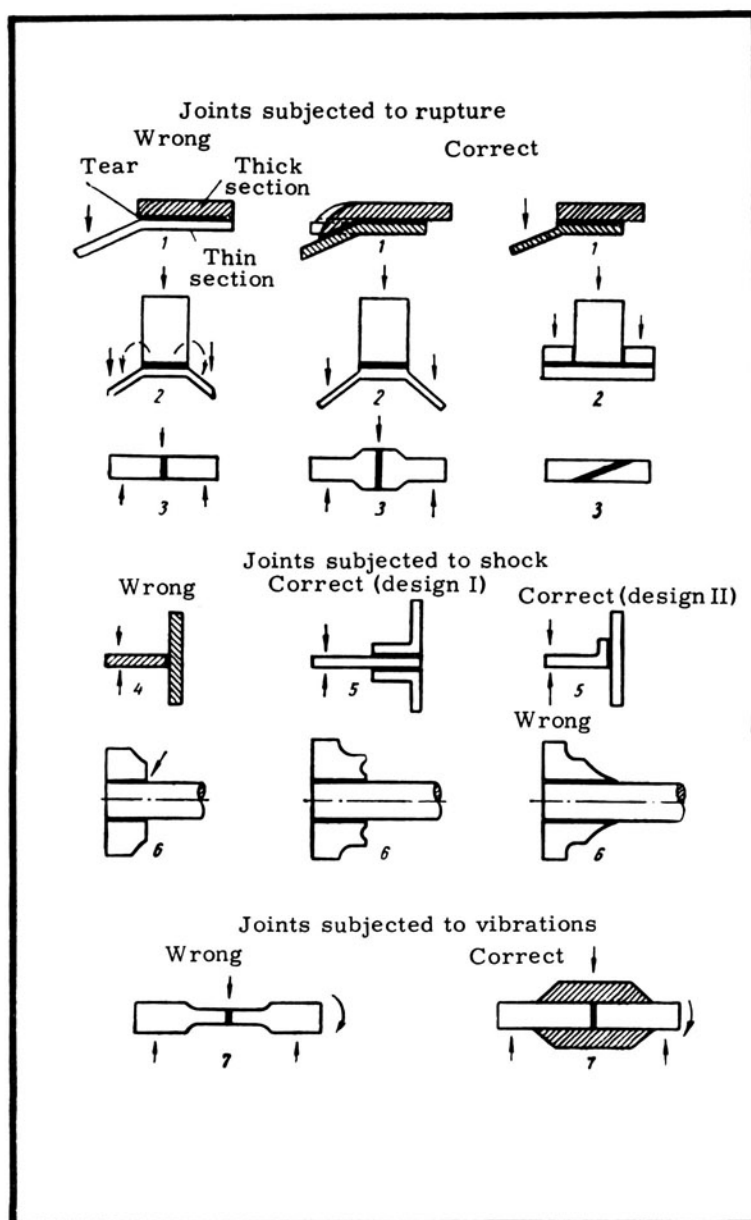


Figure 4. Correct and incorrect design of soldered joints in parts subjected to rupture, shock and vibration

In both the tubular and flat types of joint the predominant type of joint is the lap joint alone or combined with the butt or corner joint. Butt joints of type 1 (Figure 5) should be avoided, using instead internal or telescopic joints which permit us to increase the strength of the seam and to use special recesses for stress relieving, particularly in cases of impact loaded parts /6/. In Figure 5 the most frequently used designs of joints are represented (2-9).

As a result of the partial or general heating of the parts being soldered, shrinkage and warpings occur less frequently as compared with the welding process; however, an eventual occurring of such defects has not to be overlooked in designing this type of soldered joint.

In order to prevent circular (annular) shrinkage and pulling while soldering flanges to pipes, the thickness of the washer of the flange has to be greater than the wall thickness of the pipe involved; in soldering thin-walled vessels, the thickness of the shell should be a little greater than that of the bottoms.

Openings of regular geometric form corresponding to the 3rd or 4th class of accuracy, should be bored only after soldering, in order to avoid changes in their sizes due to shrinkage. Soldering of sockets to pipes can be done only when coincidence of their center lines does not require a greater accuracy. Threads requiring 4th or 5th class (USSR STANDARDS) accuracy should be cut after soldering. If an accurate coincidence of the center lines during soldering of pipes is required, allowance has to be made for their boring after soldering.

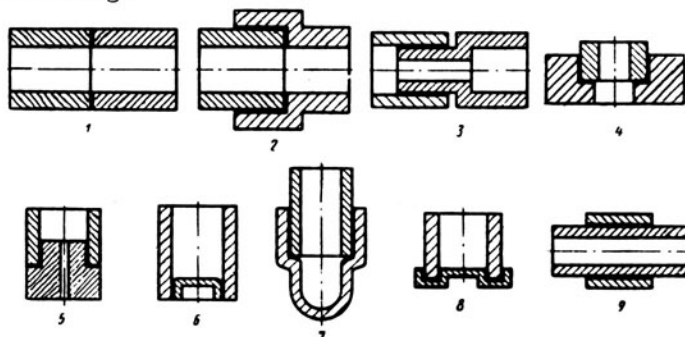


Figure 5. Design of some tubular soldered joints

§ 3. Design Features of Tee and Corner Joints on Parts in an Intersected Position

Corner and tee joints are not so frequently used as tubular or flat joints. The strength of the tee and corner joints is dependent on the correct design of the soldered seam, and increases with the increase in area of the soldered face just as in the case of tubular and flat soldered joints. Therefore, the joints 1, 2, 5 and 6 (see Figure 6) have a reduced strength and are seldom used. Joints of type 1 are used in ribbed (fin) radiators and soldered cellular constructions.

If soldered joints of higher mechanical strength are required, it is advisable to design such a soldered joint which will ensure a soldered seam of satisfactory strength. The joints of type 3, 4, 7-11 (Figure 6) afford a greater area of the soldered face /1/, /4/, /6/.

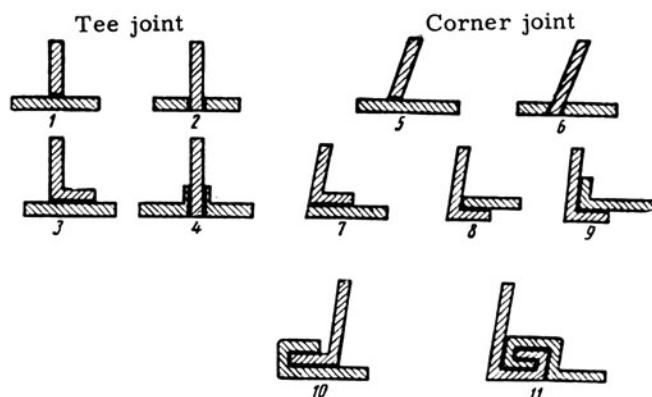


Figure 6. Tee and corner joints poorly (1, 2, 5, 6) and properly (3, 4, 7, 8, 9, 10, 11) designed

For soldering sheets and plates to crossed pipes or rods, the joints of type 1, 5, 6 and 11 (Figure 7) do not afford sufficient mechanical strength. Designs of such parts with a greater area of the soldered face and hence a greater strength, are represented in Figure 7 (2-4, 7-10, and 12-14).

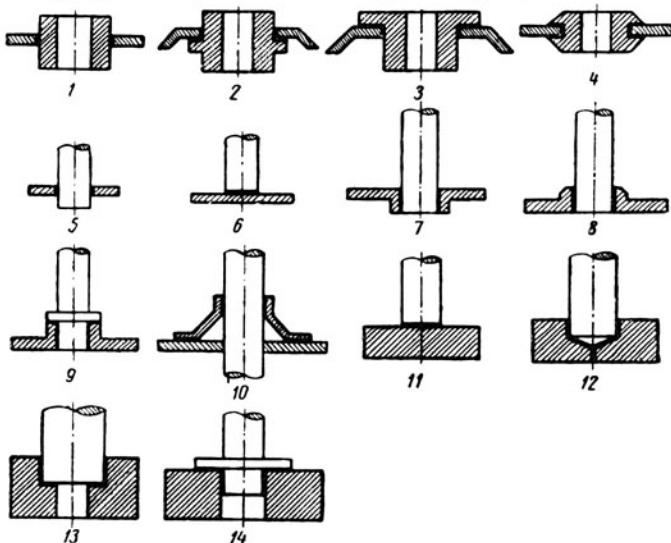


Figure 7. Correct and incorrect design of various types of soldered joints

§ 4. Design Features of Soldered Joints on Superposed Parts

The above mentioned types of soldered joints have a uniform clearance between the faces to be joined. If the contact between the soldered parts is made along a continuous line or in spots only, the clearance at different points of the soldered face will be different too; its size varies continuously from a capillary clearance to a greater width. When soldering superposed

parts, the molten solder fills the space only in its capillary part and forms a hollow in the transition to the non-capillary part of the seam.

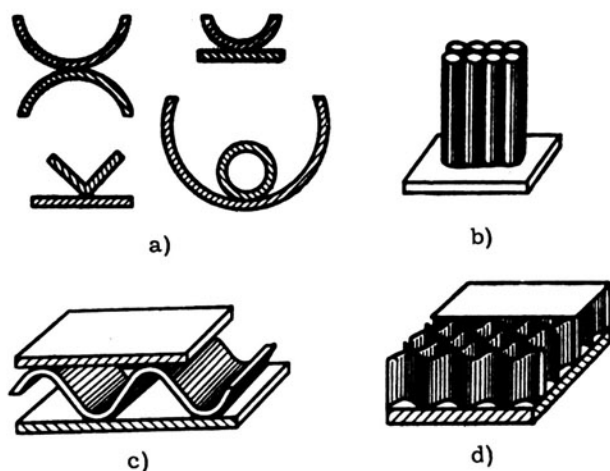


Figure 8. Types of soldered joints for superposed parts:

a—typical joints; b—core section of a soldered tubular radiator; c—three-layer lining section consisting of two linings and a corrugated filler; d—three-layer honeycomb lining section consisting of two linings and a corrugated filler.

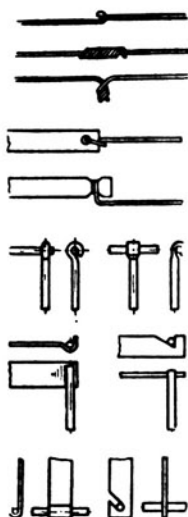


Figure 9. Examples of soldered joints for the case when both or one of the parts to be soldered is made of wire or of rods

The mechanical strength of the seam in these types of joints is usually low since the soldered area is small as compared with the cross-section of

the soldered parts. These types of joints may be used in assemblies not subjected to load, as for instance in tubular radiators or in layer sections consisting of corrugated fillers, the latter being soldered one with the other or at their contact with the lining, in soldered joints between wires and rods, etc. (Figures 8 and 9).

Soldering of superposed parts requires a sufficient amount of solder in order to secure maximum area of the joined faces.

§ 5. Recommendations for the Proper Placing of the Solder prior to Soldering

A compact filling of the joined surfaces with solder largely depends on the way it is fed into the clearance during the soldering process.

Solders are prepared in various forms: rods, wire, sheets, coils, strips, rings, disks, powder, paste or grains. In some cases, solders are applied in form of clad layers, or by electroplating, chemical coating, by an electro-erosion process or by metal-spraying (metallization). (Figure 10).

Foil or wire shaped solders are convenient for joining various tubular joints. In this case the former are applied in the shape of coils or rings externally fitted near the space between the parts or inserted into it.

The soldering ring to be slipped on the cylindrical section of the flange should be placed slightly ahead of the seam to be soldered, for if it were placed below the flange collar, the solder would not fill the space but spread over the collar (Figure 11).

In case of a gap of variable size, the solder has to be placed so as to flow from the wide to the narrow part of the gap; otherwise, the molten solder would not fill the space completely.

With a gap of uniform size it is not important whether the solder flows ahead or behind the seam; however, the solder must be placed so as to permit an unhindered escape of the air from the gap during the flow of molten solder, without forming air pockets.

In designing soldered joint for parts with a tight fit, special grooves should be provided where the solder is to be inserted before soldering (Figures 12 and 13). So for instance, when soldering a cylindrical threaded washer, several borings throughout its body will serve for feeding the solder to the seam.

When inserting the foil-shaped solder into the space between the adjoining faces, proper air drains (ventholes) are to be provided and a tight adherence of the solder to the adjacent faces in applying pressure must be assured. Sketches 4 and 6 on Figure 14 show correct and incorrect placing of solder before soldering.

Brittle solders are used in form of more or less coarse cuttings. If fixing of the solder in the space presents some difficulties, it is advisable to obtain special soldering sticks or strips by pressing soldering powder with a cementing material previously diluted in a volatile solvent, which burns out during the soldering process. Pieces of solder may also be applied by pasting with fluxing paste.

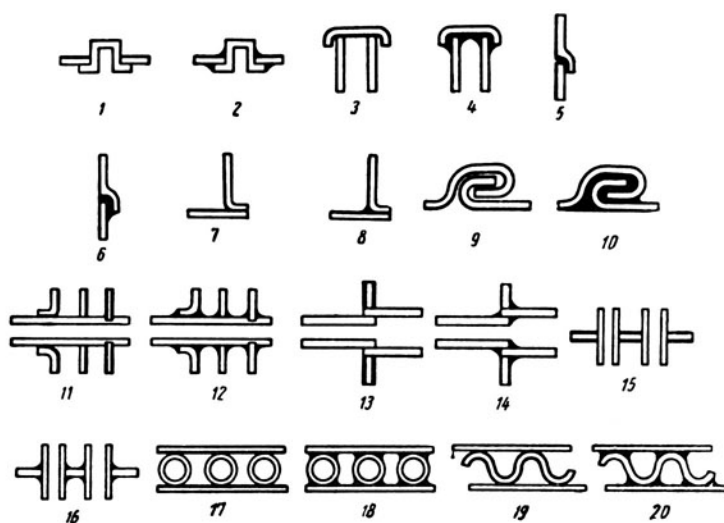


Figure 10. Designs of solder-clad sheets: before soldering (1, 3, 5, 7, 9, 11, 13, 15, 17, 19) after soldering (2, 4, 6, 8, 10, 12, 14, 16, 18, 20)

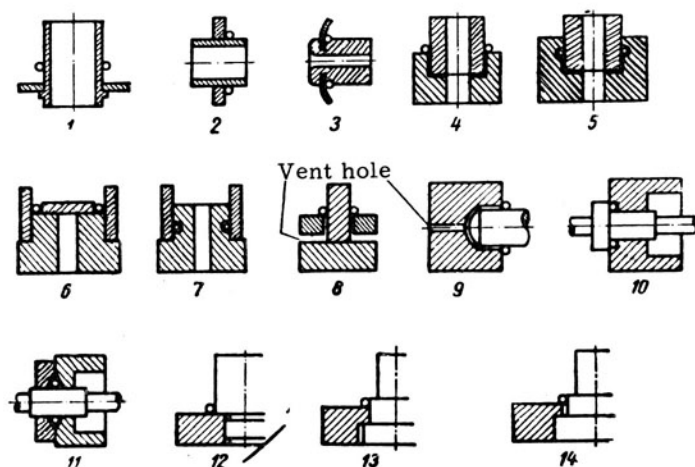


Figure 11. Placing of wire ring-solders before soldering; correct: 1-11 and 14; incorrect: 12 and 13.

Since soldering alloys have a relatively lower melting point as compared with the base metal, the properly chosen design of the joint should prevent previously made joints from being destroyed during repeated heating of the parts prior to the stepped soldering. It is therefore necessary to provide ample distance between the soldered seams. For bath and furnace soldering or for soldering in several stages, it is advisable to apply solders with different melting points.

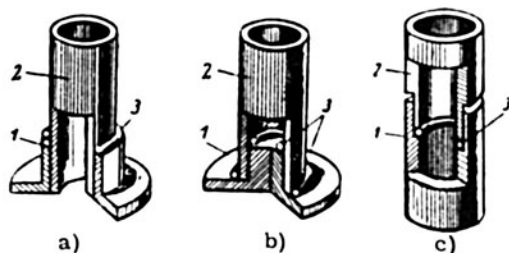


Figure 12. Placing of wire-ring solders 3 before soldering:

a—soldering of tubing 2 to flange 1; b—soldering of tubing 2 to the blind flange 1 (external and internal feeding of solder required by the large area of seam) c—soldering of tubing 2 to tubing 1.

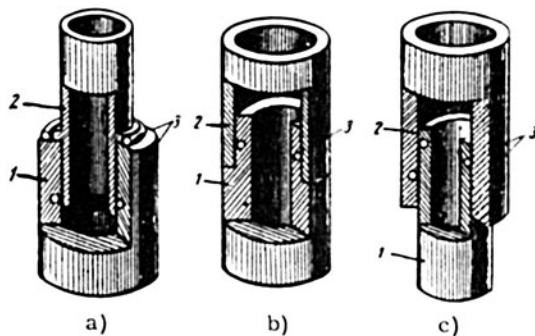


Figure 13. Inserting the solder 3 in the feeding grooves of the parts 1 and 2 soldered by local heating:

a—external heating of the joint; b—, c—internal heating of the joint.

In designing soldered joints, the state of preparation of the surface, the method of assembling the parts to be soldered as well as the methods of placing the solder on the seam are to be taken into account. Some information in connection with this can be found in Chapter X, § 1.

Soldering is often the cheapest and most feasible, and in some cases the only method which cannot be replaced by a welding process, e.g. in joining metals to nonmetallic materials, such as ceramics, glass, etc; in joining very thin parts of fine jewelry work; in applying very fine and complicated joints to thin wires, tubes or sheets; in connecting parts having different sizes or walls of different thickness. The use of soldering instead of welding may prevent, in many cases, formation of crystallizing cracks which usually appear during the welding process due to melting at temperatures above the solidus.

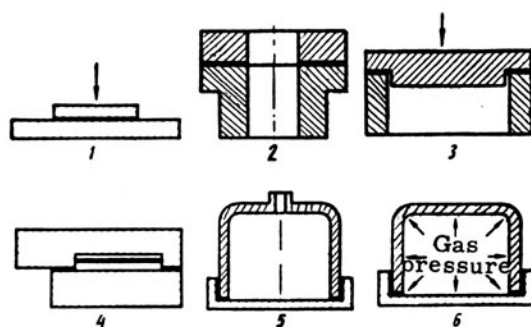


Figure 14. Different methods of placing foil-shaped solders before soldering:

correct: 1-3, 5; incorrect: 4, 6.

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Chapter II

SELECTION OF PROPER SOLDERING CLEARANCES, AND STRENGTH OF SOLDERED JOINTS

Parts should be designed with the requirements of the soldering process in mind, since compactness, tightness and mechanical strength of a soldered joint to a great extent depends on the correct choice of the soldering clearance. An incomplete filling of the capillary space with molten solder may be a result not only of poor technique (incorrect choice of temperature and duration of the soldering process, insufficient preparation of the surface to be soldered and poor quality of the flux), but may also be caused by a poor design of the soldering joints and by an incorrect selection of the clearance between the adjacent faces.

A compact filling of the space between the parts to be soldered is indispensable but not sufficient for obtaining a soldered joint of maximum strength. For a given matching of the base metal with its solder, the strength of a tight joint depends on the size of the capillary clearance between the parts.

Despite the importance of the correct size of the clearance for the resulting joint, so far there do not exist any systematical investigations on this subject. The clearance between the parts to be soldered is still chosen mainly on an empirical basis. Studies dealing with problems of soldering usually present a schematic diagram of the dependence of the tensile strength on the thickness of the soldered seam, in the form of a curve with a maximum, corresponding to a certain seam thickness.

In soldering stainless steel with a quaternary silver solder (Ag 50 %; Cu 18%; Cd 16.5% and Zn 15.5%), Leach has found first that the maximum strength of the soldered joint is obtained with a soldered layer 0.04 mm thick. Joints having a soldered layer of a larger or smaller thickness are less resistant /1/. Such a dependence was revealed by Case when investigating steel butt joints soldered with a silver solder /2/. This variation of the strength with the thickness of the soldered layer is also quoted in many studies on soldering process.

According to other data on this subject, there is not always a straight dependence of the strength of a butt-soldered joint on the thickness of the soldered seam.

Investigating the mechanical strength of butt joints in low-carbon steels, Brooker and Beatson did not notice any visible variation of the strength with the seam thickness. According to these authors, the strength of a butt-soldered joint should equal that of a cast solder /3/.

Coxe and Setapen /4/, as well as Bredz /5/ carried out investigations on the mechanical strength of butt joints of different steel grades, soldered with a quaternary silver solder of copper, with a pure silver solder, with a eutectic Ag-Cu solder and with a magnesium alloy containing 15 % Ag. They have shown that the strength of the soldered joint increases with the decrease of the space between the parts. The strength of butt joints soldered with very narrow soldering clearances, approaches the strength of steel, though failure occurs along the cast solder. This fact has been revealed also by Buehler and Colbus /6/.

Such seemingly strange occurrences may be explained by the fact that during the stretching test of a specimen taken from a soldered joint with a thin soldered layer, reduction of cross area of the specimen is hindered due to the development in it of a volume-stressed state. Such a retarding action on the development of the plastic deformation also results from a sharp notch, cut on the tensile-test specimen subjected to plastic deformations.

Tests on steel joints soldered with low-melting solders may show an increase in strength twice as large as that of the strength of the soldering alloy /5/.

On lap joints similar tests have not yet been carried out. The above mentioned trials permit us to draw the conclusion that the strength of a lap joint varies with the size of the clearance in the same manner as in butt joints.

For a given seam thickness, the strength of the butt-solder joint depends on the compactness of the solder in the seam, on the strength of the bond with the base metal or alloy, on the degree of alloying of the soldering metal in the seam, and on the retarding action of the volume-stressed state.

As practical experience has shown, maximum thickness of soldered joints is achieved at a definite size of the gap between the parts. An incomplete filling of the gap with molten solder due to very narrow clearances, may cause appearance of cavities in the soldered seam. Soldering of a limited number of alloys only permits us to obtain tight seams at a very small clearance, as for example in soldering copper to steel.

Leakiness of a soldered joint at a relatively large clearance is usually connected with reduction of solubility of the gases evolving during solidification of the molten solder, which in many cases leads to porosity of the seam.

The optimal size of clearance which determines the optimal strength of the soldered joint is dependent on the soldering temperature. Studying the soldering process with soft solders, Nightingale /7/ noticed that the optimal thickness of the seam, assuring an optimal strength of the resulting joint, varies hyperbolically with the soldering temperature. The optimal size of the clearance also depends on the chemical composition of the solder and the base metal of the parts to be soldered.

From soldering practice optimal sizes of clearances for soldering various metals with commercial grade solders were established. Some data on adequate clearances may be found in Table 1.

As shown in the above-mentioned table, the clearance for soldering of aluminum alloys is slightly larger than for soldering copper alloys and steel. This may be explained by the great reacting capacity of the solders which are required for soldering aluminum alloys.

Table 1

Clearances for soldering various metals

Type of solder	Clearance for the base metal, in mm.				Remarks
	Copper	Copper alloys	Steel	Aluminum alloys	
Copper	-	-	0.04-0.075	-	/3/
Copper	-	-	0.001-0.050	-	/8/
Brass	0.075-0.40	0.075-0.40	0.05-0.25	-	/3/
Brass	0.075-0.30	0.075-0.30	0.12	-	/9/
Copper-phosphorous	-	0.08-0.30	-	-	/3, 10/
Copper-phosphorous	0.02-0.10	0.025-0.12	-	-	
Silver-copper-phosphorous	0.06-0.30	0.055-0.30	-	-	/3/
Silver	0.03-0.25	0.03-0.25	0.025-0.15	-	/3/
Silver	-	0.05-0.07	0.03-0.08	-	/9/
	-	-	0.025-0.075	-	/11/
Silver	-	0.10	0.05-0.07	-	/11/
Silver	-	-	0.12-0.05	-	/12/
Silver	-	-	0.15-0.25	-	For laps less than 6 mm
Silver with cadmium and zinc	-	-	≤ 0.25	-	/13/
	-	-	0.25-0.60 (stainless steel)	-	For laps more than 6 mm
Fusible	-	-	0.2-0.75 on both sides	-	/12/
Alumin. alloys	-	-	-	0.10-0.25	/9/

The interdiffusion between copper, copper alloys and the required solders is considerably less intensive than in soldering aluminum; therefore, in soldering such metals, the clearance is smaller than in soldering aluminum alloys. The smallest clearance is required for soldering steel alloys, due to the relatively low rate of diffusion in the molten solder as compared with the rate of diffusion of aluminum and copper alloys into molten solders.

Raising of the soldering temperature is associated with an increased rate of the chemical interaction between the solder and the base metal. At high temperatures, the interaction between the soldering alloy and the base metal is extremely intensive; for soldering operations with the same solder but at a lower temperature, it is therefore necessary to reduce the clearance below its usual optimum value.

To prevent such a strong interaction between the solder and the base metal, soldering is usually performed at a temperature only 25-40°C higher than the liquidus temperature; in certain cases (with some silver solders), the soldering temperature may only slightly exceed the temperature of the effective range of crystallization.

The size of clearance for assembling the parts to be joined, differs

from the soldering clearance and depends on the coefficient of thermal expansion of the parts involved as well as on the method of their preheating.

In soldering parts of the same material with approximately the same mass, the clearance chosen at room temperature is kept at the soldering temperature, too.

When soldering parts of different materials, the clearance prescribed for assembling may vary considerably. Of particular importance is the difference in thermal expansion when soldering tubular or other joints. If the material of the inner member of the joint has a greater coefficient of thermal expansion than the external member, the clearance will decrease under the effect of heating. If on the other hand the material of the inner member has a smaller coefficient of thermal expansion than the outer member, the clearance will increase while heating the parts. Therefore, when selecting the size of clearance between parts of different alloys or metals, the difference in coefficients of thermal expansion as well as modifications of the clearance during heating should be taken into account.

The size of clearance is liable to undergo essential variations even in soldering parts of the same material if they are preheated at a varying rate. For instance, in soldering heavy pipes provided with small collars, rapid heating of the latter may cause a sudden increase in the size of clearance between the pipes heated to a lower temperature and the collar heated to a more elevated temperature.

A difference in the volume of the parts to be soldered may also produce important variations of the size of clearance even in heating parts of the same alloy or metal to the same temperature; the larger the radius of the inner part, the greater should be the clearance between the inner and the outer part for assembling them before soldering.

A significant difference in the coefficient of thermal expansion of soldered parts of heterogeneous materials may sometimes cause the occurrence of large internal stresses and even cracks in the soldered seam after its cooling. In order to remedy this, the soldering clearance should be enlarged.

In a soldered seam of adequate thickness, the internal stresses may be relieved to a great extent; on the other hand soldered seams with thick soldered layers are less resistant.

For soldering parts of different metals, multilayer insertions of alloys of different coefficients of thermal conductivity may be used, as they assure a smooth thermal expansion in the soldered seam [14].

The strength of a soldered seam depends not only on the size of the clearance but also on its position relative to the direction of the stress. Furthermore, in a lap joint the mechanical strength of a soldered seam can be greatly enlarged by increasing the area of the soldered face.

The size of the overlapped section (the lap) is chosen according to the strength of the base metal and to the area of the cross section of the part to be soldered in its thinnest section.

The formula for determining the size of the overlapped section can be written as follows:

$$\sigma_b S = \tau_s FK,$$

where σ_b = ultimate strength;

S = area of the weakest cross-section of the soldered joint;

τ_s = shear strength of the lap joint;

F = area of the overlapped surface;

K = safety factor (~ 5).

In a butt joint the area of the soldered face is given by the area of the cross-section of the parts to be united.

The mechanical strength of the soldered joint depends not only upon the state of tension of the filler metal deposited in the gap, but also on the changes in composition and construction of the solder as a result of diffusion processes between the filler metal (solder) and the base metal. Data on the strength of copper parts butt-soldered with a lead, tin and zinc alloy are presented in Table 2.

Table 2—

Mechanical strength of cast metals and copper parts, butt-soldered with lead, tin and zinc alloys

Type of solder	Ultimate strength of the solder, kg/mm ²	Ultimate strength of the copper base metal, kg/mm ²
Lead.....	1.3	1.3-4.0
Tin.....	1.4	5.7
Zinc.....	13	3.8

Lead does not form an intermediate layer; it adheres to copper only in a very thin layer. The strength of the lead soldered joint equals the strength of the lead itself or even exceeds it; this seems to be due to the strengthening influence of the area of the soldered faces. Tin soldered to copper, forms with the latter, solid solutions and chemical compounds. The greater hardness of a tin-soldered joint, as compared with the hardness of tin, is a result of the stressed state in the gap and of the hardening of the solder itself owing to its changed composition. Zinc soldered to copper, forms with the copper solid solutions and intermetallic low-plastic phases. The lower plasticity of the molten solder in the gap between the tin-soldered copper parts, apparently caused a reduction in strength of the soldered joint as compared with the strength of the zinc itself.

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Section Two

PHYSICS AND CHEMISTRY OF SOLDERING AND ITS INFLUENCE ON THE PROPERTIES OF THE SOLDERED JOINT

Chapter III

PROCESSES ASSOCIATED WITH THE FORMATION OF THE SOLDERED SEAM

§ 1. Filling of the Gap Between the Adjoining Faces and the Processes Involved

The formation of a soldered joint is accompanied by a number of transformations in the liquid and solid state of the metal involved.

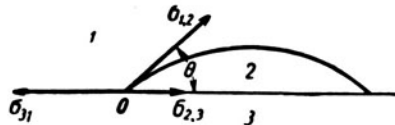


Figure 15. Equilibrium diagram of a liquid droplet on the surface of a solid

A strong bond between the solder and the base metal to be joined, requires first of all a close contact between them. The solder, melting under the action of heat, penetrates into the gap due to the attraction of capillary forces and sometimes due also to gravity. In braze welding, the filling of the gap with liquid solder is effected mainly under the action of gravity (wettability). Wetting is a decisive factor assuring a tight contact between the solder and the metal to be united.

Liquid solders are unable to wet a base metal surface covered with a film that forms a non-metallic bond with the base metal. Therefore, it is necessary to remove all matter having a non-metallic bond with the base metal as dirt, grease, sulfurs, etc before soldering.

Interaction between the solder and the base metal may occur in open air, in a vacuum, in an inert (neutral) or reducing atmosphere or under a layer of molten flux; consequently, the soldering process is essentially a three-phase process. Under given conditions, between the droplets of molten solder and the base metal an equilibrium is established, determined

by the surface tension $\sigma_{2,3}$ on the boundary layer between the molten solder and the base metal, by the tension $\sigma_{3,1}$, on the boundary layer between the base metal and the gaseous atmosphere or the flux and finally, by the tension $\sigma_{1,2}$ between the molten solder and the gaseous atmosphere or the flux:

$$\sigma_{3,1} = \sigma_{1,2} \cos \theta + \sigma_{2,3}.$$

The angle θ (Figure 15) termed angle of contact or interface angle, varies within the limits from 180° to 0° ; on the other hand, the expression, $\cos \theta = B$, characterizes the ability of the solder to wet the base metal.

If B and θ are within the limits of $0 < B < 1$ and $0 < \theta < 90^\circ$, the base metal will be wet by the molten solder ($\sigma_{2,3} > \sigma_{1,3}$); if B is negative and the angle of contact θ is greater than 90° , i.e. $-1 < B < 1$ and $90 < \theta < 180^\circ$, then the base metal will not be wet by the solder.

Table 3 presents data on the magnitude of the interface angle of liquid tin and eutectics spread over copper /1/. It results from these data that eutectic has a better wetting action on copper than tin.

Table 3

Interface angle of molten tin and Pb-Sn eutectic, spread over copper under a layer of flux (90 % of zinc-chloride and 10 % of ammonium chloride)

Type of solder	Temperature, °C	Angle of contact, degrees	Type of solder	Temperature, °C	Interface angle, degrees
Tin	250	50	Eutectic Sn-Pb	200	35
"	300	40	"	260	0

Wetting of the base metal with molten solder always leads to a metallic bond in the form of a solid solution or a chemical combination. Metals unable to form among themselves solid solutions or chemical compounds do not wet each other and form immiscible liquids; the molten solder, being on the surface of the solid base metal gathers in droplets. This is true of the following groups of metals: Fe-Ag; Fe-Pb; Cu-Pb; Fe-Cd; Fe-Bi; Cu-Bi; /2/, /3/, Cu-Mo; Cu-W; Cd-Al; Pb-Al. It is impossible to solder the low-melting metal of these groups with a fusible metal; soldering can be carried out only by adding to the fusible metal a chemical element with chemical affinity for either metal of the corresponding couple. So, for instance, high quality soldering of tungsten is impossible with pure copper but alloying copper with iron or nickel (V~1 %) may assist in filling the gap between the parts and in ensuring a strong soldered joint, as iron and nickel are able to form a strong metallic bond with copper and tungsten.

V.V. Frolov /4/ has shown that wetting of a solid metal by a liquid metal depends on the nature of the chemical bond between them and particularly on their intersolubility.

Mutually immiscible metals practically do not wet each other (e.g., a droplet of molten cadmium on aluminium, of molten lead on aluminum or of molten bismut on iron). Large angles of contact ($120-150^\circ$) are due (in this case) to the dissolving of impurities of the solder in the base metal.

Intersolubility of both metals (solder and base metal) increases the wetting action of the liquid phase on the solid phase whereas the interface angle is diminished. The interface angle and the wettability of the metal depends to a certain extent on the surface tension of the liquid phase but is not determined by the latter. Figure 16 illustrates the variation of the

interface angle during wetting of the surface of ShKh15-steel parts by lead-tin alloys. Lead has a poor wetting action on steel as it does not form visible solid solutions in steel; tin, added in small quantities improves wetting of steel. Wettability is not in a straight dependence on the surface tension. Surface tension of Pb-Sn alloys varies gradually and monotonously (Figure 17) /5/. The strong influence of tin on the wettability of steel by lead is connected with the chemical interaction between tin and iron and with the ability to form with iron solid solutions and chemical compounds (FeSn_2).

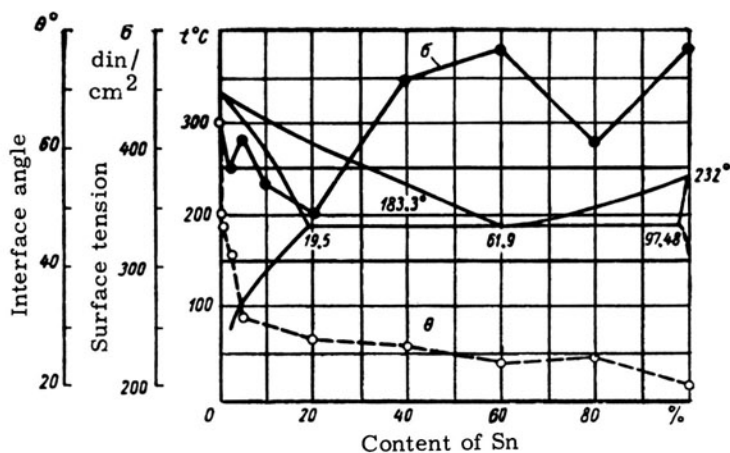


Figure 16. Variation of the interface angle θ in wetting a steel surface by a Sn-Pb alloy, as compared with the equilibrium diagram and the variation of the surface tension σ of the alloys of the same system

Wettability is also greatly assisted by absorption processes occurring on the surface of a solid; this is mainly connected with the variation of free energy on the surface of the bodies.

Instead of wetting by a molten solder, the contrary phenomenon, interruption of the wetting action owing to the diffusion of atmospheric oxygen into the molten solder /6/ is liable to occur.

Spreading of molten solder on the base metal to a certain extent characterizes its ability to fill completely the space between the parts to be joined. Spreading of molten solder on the solid base metal depends on the roughness of its surface. The rough surface of the basic metal forms a sort of capillary channel through which molten solder flows. On the other hand, on a smooth, polished surface, spreadability of molten metal is very small.

The different degrees of roughness of the parts to be soldered have a visible influence on spreadability of molten solders having a reduced interaction with the base metal. At a pronounced physical and chemical interaction, the irregularities on the surface are easily dissolved by the molten metal, which breaks the continuity of the capillary channels. This may

occur when aluminum alloys are soldered with aluminum solders, particularly if the latter have a large zinc content (as known, zinc has a strong dissolving effect on aluminium). Therefore, the effect of surface roughness on the spreadability of a solder on its base metal decreases with the increase in the soldering temperature since the dissolving capacity of liquid solder increases at the same time.

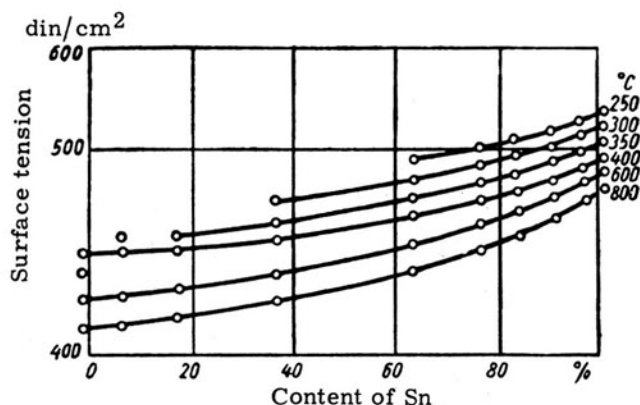


Figure 17. Relation between surface tension of a Pb-Sn alloy and heating temperature (250-800°C)

This has been clearly confirmed by special tests.

Thin copper, 1Kh18N9T-steel and AMn alloy disks have been divided in four segments, the surface of each being pre-treated by polishing, steel-brushing, cleaning with emery-paper cloth and pickling (etching). The AMn-alloy segment was etched with a 10% aqueous solution of NaOH and then purified with a 10% aqueous solution of HNO_3 . A piece of alloy of 0.5 cm³ in volume was subsequently inserted in the center of the disk, covered with flux and then introduced into a crucible together with the disk, where it was heated to the soldering temperature for 5 minutes. The crucible was then opened and after the molten solder was solidified, the tinned disk was withdrawn from the crucible and the residue of flux cleaned off. Spreadability of a POS40 alloy on the polished segment is much smaller than on segments previously treated by other methods. This did not occur in other cases. Spreadability of these alloys was best on steel-brushed surfaces. Spreadability of a P-250 solder on a AMn alloy depends only slightly on the pre-treatment of the surface. The PSr40 solder had a reduced spreadability on the 1Kh18N9T-steel disk cleaned with emery paper as the abrasive grains reduced the wettability of steel, whereas the wettability of the AMn alloy by the 34A solder (on an aluminum base) was not affected. Directed spreadability is intensified by parallel capillary scratches, formed during surface treatment of test specimens.

Spreadability of molten solder on a base metal or alloy, associated with their wettability is a very complex property. As it will be shown, spreadability does not depend on other, well known fluid properties, particularly important for the casting practice of alloys as, fluidity, viscosity,

and surface tension. Spreadability and fluidity are only slightly interdependent. Spreadability is the property of a molten metal or alloy to modify its shape while on the surface of another metal or alloy or in the gap between them. This change of shape often depends on the force of gravity but mostly on the interaction between the free energy of the molten solder and the energy of the solid alloy or metal to be soldered.

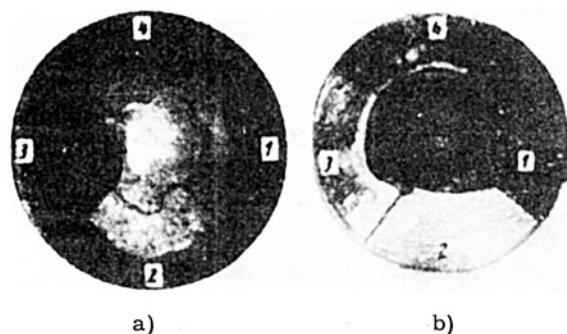


Figure 18. Spreadability of a PSr40 KN solder on stainless steel (a) and of a P-200 solder on a AMn aluminum alloy (b) with differently pre-treated surfaces:

1—polished; 2—etched; 3—cleaned with fine-grain emery-paper; 4—steel-brushed.

Fluidity of a crystallizing liquid is its property to flow, mainly under the action of gravity through vertical or inclined channels having solid walls. As a rule, the solid walls of these channels do not chemically interact with the liquid; their influence on fluidity is confined particularly to elimination of heat or gases.

The phenomenon of fluidity becomes important in some rare instances of soldering when the solder penetrates into the gap in an incomplete molten state, i.e. in a state of partial crystallization.

Thus, fluidity depends on the nature and form of crystallization of the metals and alloys involved. Two basic laws governing the change of fluidity of alloys have been established:

1. Fluidity varies inversely with the range of crystallization. Maximum fluidity occurs in pure metals and their eutectics, minimum fluidity occurs in alloys with the widest range of crystallization.

2. Fluidity depends on the form of the growing crystals of the molten alloy. Greater fluidity occurs when rounded crystals are formed on a continuous front line; lesser fluidity, when ramified dendritic crystals are formed.

Bochvar and Kuzina /7/ have shown that these basic laws depend upon how much the crystallizing portions of the alloy impede the efflux of the molten portion of that alloy. When ramified dendritic crystals are formed, the molten alloy is jammed in the interaxial space, whereas in case of a continuous front-line crystallization, the molten alloy tends to flow more freely.

Figure 19 illustrates the variation of fluidity of a Sn-Pb alloy /8/.

The dependence of spreadability of alloys on their composition is similar in form to that of fluidity but with a different origin.

Spreading tests have been carried out, with the molten solder overheated above the liquidus by 60, 100, and 150°C.

Results of such spreading tests for Sn-Pb alloys on copper and steel are shown in Figures 20 and 21.

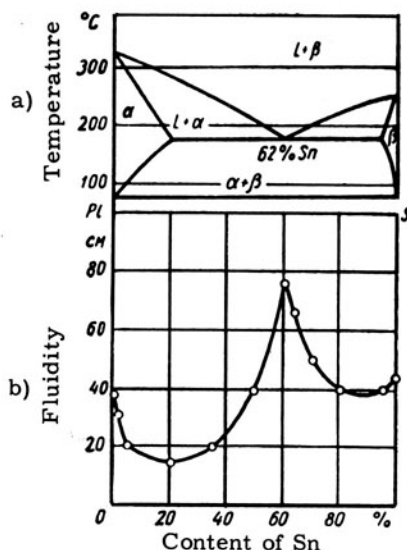


Figure 19. Dependence of fluidity of Pb-Sn alloys on their composition and structure:

a—equilibrium diagrams of Pb-Sn alloys; b—fluidity of Sn-Pb alloys.

These tests reveal the peculiar nature of spreadability; though it is connected with wettability and surface tension of the liquid, its characteristic change does not depend only on the change of surface tension. Actually, the surface tension of a Sn-Pb alloy [5] heated in a hydrogen atmosphere, decreases with the increase in concentration of lead (Figure 17). Such a smooth change has been noticed when establishing the technological characteristics of Sn-Pb alloys as related to the surface tension, namely, the height of the rise of the molten alloy in the capillary space between parallel aluminum walls, and the filling time of the capillary space [9].

Variation of surface tension with temperature also occurs gradually without any peculiarities (without an extremum).

Spreadability does not depend on viscosity of liquids either. Viscosity of liquids is only connected with the mobility of the atoms of the respective fluid, whereas spreadability depends on the inner mobility of the fluid as well as on the mobility due to the surface energy (free energy). Apart from this, viscosity of Sn-Pb alloys exhibits no other peculiarities at the eutectic point (Figure 22). The increase in viscosity of eutectics, revealed by S.V. Sergeev and E.V. Polyak, depends both on the presence of oxide films

on the surface and the method of measuring viscosity /10/.

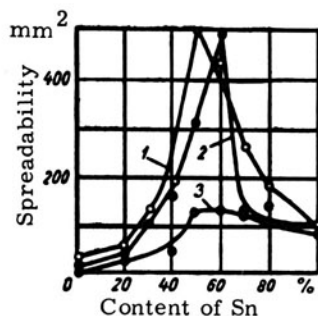


Figure 20. Variation of spreadability of Pb-Sn alloys on copper when heated above the liquidus:

1, by 20° C; 2, by 60° C; 3, by 150° C.

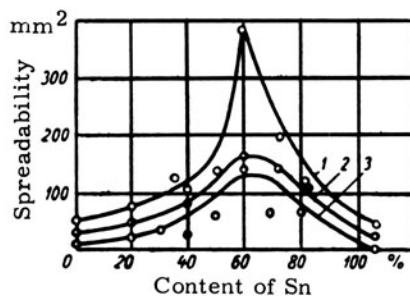


Figure 21. Variation of spreadability of Pb-Sn alloys on steel when heated above the liquidus:

1, by 20° C; 2, by 60° C; 3, by 150° C.

This unusual behavior in the spreadability of molten alloys seems to be connected with the peculiarities of the variation of the structure of molten solders with the heating temperature, as well as with the state of the surface of the solid. Spreadability should undoubtedly be linked with the surface tension which prevents spreading of the liquid droplet as well as with the free energy on the surface of the solid.

As a result of chemical interaction between the molten solder and the base metal, the composition of the solder changes and leads to variation of spreadability. As a rule, dissolving the base metal by the molten solder produces modification of its viscosity, surface tension and range of crystallization. Dissolving of the base metal in the liquid solder mostly increases the liquidus and the solidus of the alloy in the soldered seam. All these phenomena are liable to impede spreading of the molten solder and its penetration into the gap between the members of the joint. In case of a

strong interaction between the base metal and the molten solder, the clearance should be larger than in the case of a reduced interaction.

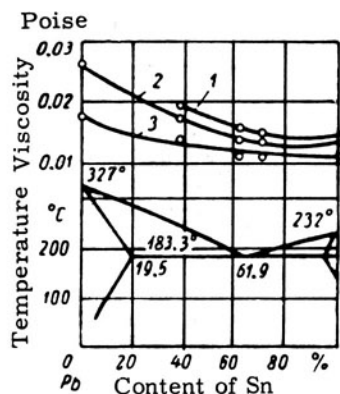


Figure 22. Viscosity of Pb-Sn alloys at different temperatures, as compared with the equilibrium diagram for this system:

1, at 300°C; 2, at 360°C; 3, at 500°C.

The reduction of spreadability of the molten solders, sometimes noticed at temperatures above a certain limit, may be explained by the chemical interaction between the solder and its base metal; at these temperatures, the chemical processes prevail over the physical processes.

Table 4 presents testing data on surface tension of tin lead and Sn-Pb eutectics (slightly above the melting point), covered with different kinds of fluxes. Various fluxes while in contact with the molten metal and eutectic, changed their surface tension. Of particular interest are the data referring to the action of colophony dissolved in alcohol. Until recently it was admitted that colophony fluxes prevent only oxidation of solders without interacting with them, but as it has been shown, this neutral flux also lowers the surface tension of the molten Sn-Pb alloy.

Table 4

Surface tension of tin, lead and Pb-Sn eutectic at temperatures slightly above the melting point / 1/

Types of metal	Surface tension with different fluxes in dyne/cm ²			
	Hydrogen	Colophony	Zinc chloride and ammonium chloride	Tin chloride
Tin.	550	456	422	342
Pb-Sn eutectic...	490	390	331	-
Lead	440	316	-	-

Some theoretical aspects of the filling of the gap with molten solder in connection with its capillary properties have been studied by Latin /11/ and Earle /12/.

The external view of a soldered surface often has an essential importance. When soldering metals in a wide range of crystallization, the surface of the soldered joint becomes rough and irregular, due to the dendritic development of growing crystals between which the more fusible portion of the molten solder is solidifying. As a result of contraction phenomena, the surface of the joint becomes rough, whereas in solders of eutectic composition the surface becomes smoother.

Irregularity of the surface of the soldered joint is dependent also on the magnitude of the crystallites (large crystals). Solders with large crystallites form an irregular surface while small crystallites produce a smoother one.

The filling of the gap with molten solder is not merely a physical process, particularly when the solder has a wide range of crystallization. Such solders with a liquidus above the solidus of the base metal, when used in a soldering operation, may lead to an incomplete filling of the gap between the parts to be soldered. Incomplete filling with molten solder is due to changes in composition of the solid phase. Actually, in certain cases of soldering (particularly in furnace soldering) the capillary space is first filled with the more fusible phase of molten solder. As a result, the solid phase of the solder which remained outside the gap, undergoes changes in its composition; the range of crystallization of the remainder will thereby differ from the range of the original solder. In a certain stage of soldering the liquidus of the residue of the solder can be higher than the soldering temperature, thus preventing the molten solder from being drawn into the gap.

The ability of the molten solder to fill the capillary gap can be estimated by the following factors: 1. by the height to which the molten solder rises in the capillary space between the walls of the base metal, mutually located at a certain angle; 2. by the height of rise of molten solder on twisted wires of the base metal; immersed in liquid solder; /13/, /14/. 3. by the height of rise of molten solder in the gap between the two parallel metallic wires (for the purpose of the test, Rhines and Anderson /15/ used copper wires of 6 mm in diameter and 80 mm in length; the clearance was 0.18 mm).

The process of gradual crystallization is associated with changes in composition of the molten solder, rising up in the capillary space: in the upper layers the fusible constituent of the solder (sometimes a pure eutectic) is crystallized.

§ 2. Interdiffusion between the Molten Solder and the Base Metal

As a rule, under the action of the soldering process, the solid base-metal is dissolved in the molten solder.

In his study /16/ Nightingale presents data on the changes in chemical composition of liquid Pb-Sn solders and of liquid tin when small cubes of copper are immersed and "soaked" in it for an hour. It was found that, with the increase in the duration of soaking and in the temperature of the

molten solder, the amount of copper dissolved in the molten solder also increased. These are not isolated cases; so, for instance, steel and cast iron are very easily dissolved in liquid aluminum and its alloys at temperatures much higher than their melting point. Interdiffusion between the solid and liquid solder and the base metal (which is) one of the basic processes of soldering, is a simultaneous process of diffusion of the liquid or solid solder into the solid base metal. The intensity of these processes is not constant, being governed by the physical and chemical properties of the parts to be joined and by the temperature of the soldering process.

During soldering, liquid solutions may appear when such metals or alloys are joined, the components of which are liable to be mutually dissolved in the liquid state. Metals, mutually soluble in the solid state are also invariably dissolved in the liquid state. Nevertheless, some metals, though soluble in the liquid state, are insoluble in the solid state.

The assumption that the base metal is invariably dissolved by the liquid solder has so far no sufficient support by practical experience. Though a similar dissolution has been noticed in many types of soldered joints, in some cases a visible dissolution of the base metal in the liquid (molten) solder could not be observed, e.g. in soldering cadmium to iron or aluminum. Soldering is conceivable without an apparent dissolution of the joined metal or alloy in the liquid solder. This probably occurs when metals and alloys are dissolved with a solder which has a much lower melting point than the soldered alloy, in which case the diffusion is very slow and takes place in extremely narrow zones of the solder and the base metal, close to the place of mutual contact.

Formation of liquid solutions during soldering has been the subject of detailed chemical and metallographic examinations; this refers particularly to the formation of solid solutions during soldering of copper alloys with tin solders /16/.

The ability to control the process of diffusion during soldering is of prime importance in making soldered joints of required qualities. In this connection, the example of applying diffusion processes to such difficult instances as soldering of easy oxidizable multicomponent alloys, may be mentioned.

Certain alloys are liable to form heat-resistant oxides during soldering; such alloys are chromium, aluminum, beryllium or silicon alloys or heat and oxidation resistant iron and nickel alloys containing the above mentioned alloying elements. In order to reduce the oxidability of such alloys during their heating they are soldered with low-alloyed solders so that the easily oxidizable constituents (elements), before or during the soldering process, are diffused into the molten solder and their concentration on the surface of the base metal is reduced. For this purpose foil-shaped low-alloyed solders are to be used and soldering is to be performed in an inert or reducing atmosphere.

In order to promote diffusion, the soldering temperature should be as high as possible.

In this connection soldering of aluminum bronze with L62 brass solders in a hydrogen atmosphere at a temperature of 1000°C may be mentioned /17/.

This procedure permits soldering of heat-resistant and heat-stable iron and nickel alloys containing chromium and aluminum, with low-alloyed solders composed of the following solid solutions: Ni-Mn, Ni-Cr-Mn, and

Ni-Fe-Mn-Co-Cr. The so-formed relatively low-alloyed soldered seams have a sufficient plasticity and are less prone to form surface cracks or skewings than high-alloyed solders: their mechanical strength is therefore sufficiently high.

§ 3. Crystallization of the Seam During Soldering

In many instances of soldering, crystallization of the soldered seam occurs not at a definite temperature but over a certain range.

The crystallization range of alloys exhibits two distinct subranges, differing in the nature of the processes involved: 1) the upper subrange with the liquidus line as its upper boundary. In this subrange the growing solid phase is isolated by interlayers of liquid phases (the liquid-solid condition); the alloy is subjected to changes in volume without any linear contraction; 2) the lower subrange, in which the dendrites growing from the solid phase are mutually bonded forming a rigid skeleton. Starting from the binding temperature of the dendrites, any further cooling of the molten alloy will be accompanied by a linear contraction of the solid skeleton. This temperature range is termed the effective range of crystallization and is limited in its lower region by the liquidus line (the solid-liquid state). /18/ and /19/. In the upper subrange of crystallization, the alloy has a relatively unhindered movability and can fill in the gap between the parts to be joined. Therefore, soldering may be achieved even at the temperature of the upper-subrange of crystallization.

As soldering practice has shown, when certain soldering alloys, particularly such on an aluminum base are used as solders, the lower limit of the soldering temperature may be below the liquidus temperature of the solder, in cases where its effective range of crystallization (i.e. the interval of the solid-liquid state) is a very narrow one. With solders having a large range of the solid-liquid state, the soldering temperature should exceed the liquidus point of the solder. Figure 23 presents data on the spreadability of liquid Al-Si alloys in the crystallization range, on an aluminum base-metal. These alloys spread on an aluminum base-metal below the liquidus temperature, starting from a Si content of about 5-6%, i.e. when the effective range of crystallization becomes very narrow (restraint).

The temperature of the incipient coherence of the dendritic crystals depends on the composition of the alloy. Investigations in conjunction with the crystallization of eutectic binary-alloys /20/ and /21/ have shown that small amounts of alloying elements added to aluminum, reduce the temperature of the incipient coherence of the dendrites, but on appearance of a non-equilibrium eutectic the temperature rises again and attains a maximum value at a certain amount of this eutectic.

The spreadability of liquid solders at temperatures below the liquidus temperature may be illustrated by the example of silver solders /22/.

When high-melting alloys are soldered with low-melting solders, the lower limit of the soldering range is by 40-50°C⁰ higher than the liquidus temperature of the solder /23/.

The lower limit of the temperature range in soldering high-melting alloys with solders of a relative high melting-point is usually assumed to coincide with the liquidus line of the solder. Crystallization of the soldered

seam is affected by the base metal since the walls of the capillary space (gap) act as nuclei of the nascent phases in the solidifying metal. When both the soldered alloy and the solder have common phases, the crystallizing phase in the soldered seam grows from the crystals of the same phase in the base metal [21]. The phase in the base metal steadily passes into the soldered seam (the so called common crystallization). Such a formation and growth of the phases in the soldered seam is governed by the law of minimum energy required for the formation of a solid phase in liquid environment.

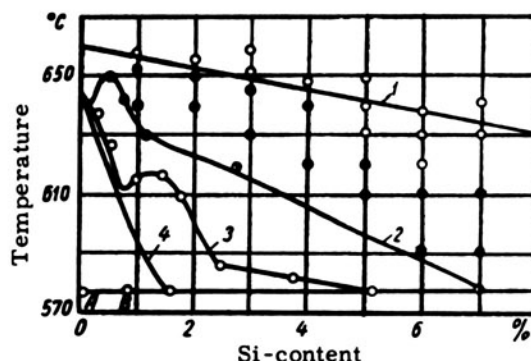


Figure 23. Spreadability of Al-Si alloys on aluminum at different temperatures: black circles-the alloys are spreading; white circles-the alloys do not spread within five minutes:

1-Liquidus of Al-Si alloys; 2-upper limit of the effective range of crystallization at a cooling rate of 400°C/min. ; 3-at a cooling rate of 2°C/min. ; 4-equilibrium solidus-line. A and B indicate composition of alloys in which a non-equilibrium eutectic is formed at a cooling rate of 400°C and 2°C/min respectively.

Common crystallization is inherent both to soldering and welding [24/, [25/ and [26/. As shown on Figure 24 grains of the D-20 alloy soldered with a B62-solder constituted nuclei of common crystallization of the solid solution of aluminum in the soldered seam. The different etching ability of the grains in the soldered seam and in the base metal is due to the different degree of concentration of the alloying elements in both the soldered seam and the base metal. Of definite importance for the growth of such a phase is the same crystal structure of two different portions of the grains.

During soldering of L62 brass to copper, the crystals of the grain portions of copper directly grow into the portions of the same grains in the solid solution of zinc in copper (brass) (see Figure 25). Annealing twins already existing in copper pass also in the soldered seam though they are typical of the deformed metal.

The process of common crystallization occurs when copper parts are soldered with tin or tin-lead solders (Figure 26). The soldered joint grows in the form of shoots into the soldered seam.



Figure 24. Common crystallization of a solid solution of aluminum in a D-20 alloy seam, soldered with a B62 solder $\times 450$

Chemical compounds, formed on the interface between the metal and the solder may form either directly from the metal during its saturation with elements in an amount sufficient to give rise to a chemical combination or they may form in the solid solution of the base metal under the action of an intense diffusive migration of atoms from the liquid solder into the metal to be joined.

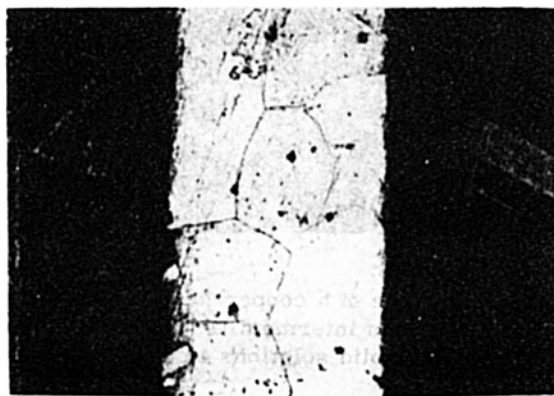


Figure 25. Microstructure of a copper joint soldered with an L62 brass solder. Enlarging $\times 300$

During soldering the first process is more frequent than the second (due to the dissolution of the base metal in the molten solder and the great rate of diffusion into the liquid metal). Chemical compounds form sometimes in the soldered seam directly from the liquid phase (in the presence of liquation processes).

Common crystallization does not occur when metals and alloys are soldered with solders which do not form common phases of the same crystalline structure. In this case the bond between them is a result only of the common diffusion into a sufficiently thin layer or of the interdiffusion between the grains of phases of a different crystal nature (e. g. soldering of lead to iron or nickel etc.).

According to A.A. Alov /24/, the process of common crystallization (termed by him mutual crystallization), takes place in all types of welding of metals and alloys but not in soldering /27/.

The above mentioned facts of common crystallization during soldering, reveal how artificially the distinction of soldering from welding is made according to this feature.

The development of the welding technique permitted us to gradually replace welding of similar metals, where common crystallization is quite frequent, by welding of dissimilar metals where common crystallization does not occur.

The crystallization range is of paramount importance in choosing the type of soldering involved. Solders exhibit a reduced deformability (capacity of deformation) in the effective range of crystallization. Displacement (skewing) of the members to be joined may lead, in the effective range of crystallization, to a local or even general destruction of the soldered seam.

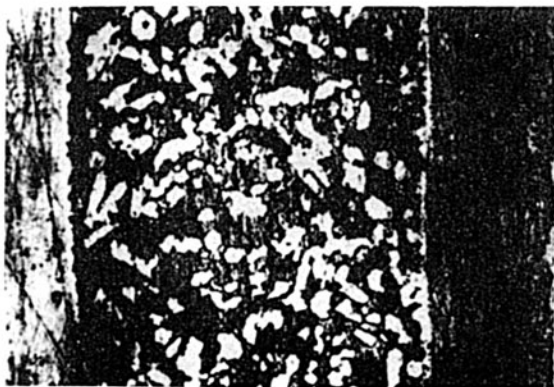


Figure 26. Microstructure of a copper joint soldered with tin solders (bright phase indicates intermetallic crystals; dark phase indicates solid solutions on a tin base) $\times 250$

The widening of the effective range of crystallization of the solder increases the danger of destruction of the soldered seam.

When applying a soldering bit (iron), the crystallization range should be a reduced one since the solder, transferred from the bit on to the seam must be in a liquid state. For instance, among the solders of the Sn-Pb

system, most suitable for dip soldering and soldering with a soldering bit, is the eutectic alloy with 62% of Sn /28/.

Friction (abrasive) soldering is more easily accomplished with solders having a large crystallization range (i.e., a particularly wide range of the solid-liquid state). For this type of soldering, solders on a Sn-Pb base with 30% Sn, are most suited.

For dip soldering, solders with a varying range of crystallization may be used: the bath of molten solder is the best source for a continuous feeding of the soldered seam. Dip soldering may also be performed with solders having a wide range of crystallization (e.g., POS18 solder).

§ 4. Formation of Solid Solutions and Chemical Compounds During Soldering

Solid solutions form in the metal or alloy to be soldered, at relatively elevated soldering temperatures and at a high rate of diffusion of the alloying elements from the solder into the base metal. The nature of this process is still more or less unknown. The process of diffusion in the solid state, can clearly be revealed, e.g. through metallographic examination of the structure of aluminum joints soldered with aluminum solders,

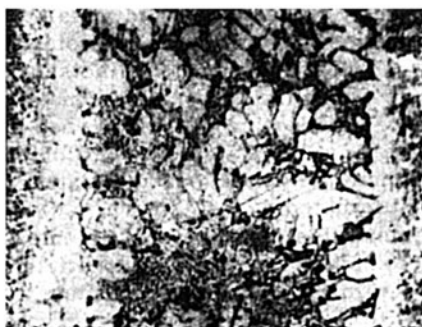


Figure 27. Microstructure of an aluminum joint soldered with a 34A solder $\times 450$

Figure 27 depicts an aluminum joint soldered with a 34A Al-Si-Cu eutectic soldering alloy. Parallel to the layer of solder, a bright area can be seen. This area is brighter than aluminum, for it represents the solid solution of silicon and copper in aluminum.

Interdiffusion of two elements is sometimes associated with formation of chemical compounds. This fact has found practical application in many processes of chemical heat-treatment. A similar diffusion is called reaction-diffusion.

Chemical compounds may appear during diffusion or reaction-diffusion respectively, but may form also upon cooling of the supersaturated solution formed during the diffusion process; in this case as a result of decomposition

of the solid solution, chemical stable or metastable compounds are formed.

As to the formation of chemical compounds during the diffusion process, different points of view have been expressed. Some authors affirm that chemical compounds form during diffusion, after the boundary layer of the solvent has attained its saturation limit, whereas according to others, during the mutual contact of the diffusing metals, chemical compounds may be produced directly on the interface (border of separation) between the metals involved, regardless of their mutual solubility /29/.

These chemical compounds always should correspond to the equilibrium diagram of the mutually diffusing metals. Actually, a similar diffusion, particularly in the Cu-Zn system, could be noticed. The composition of these compounds must not be close to that of the solvent metal /29/.

The phenomenon of metastable equilibrium during diffusion in the solid state has been revealed also in other systems (Ag-Cd, etc.); it occurs during formation of metastable phases which do not correspond to the equilibrium diagram, e.g. in various processes of decomposition of solid solutions.

During interdiffusion between high-melting and low-melting metals in the liquid state, one may expect formation of phases which are in a stable or metastable equilibrium with the solid metal; on the other hand formation of metastable phases is liable to occur in the high-melting metal during its crystallization, in which case these phases do not correspond to the equilibrium diagram.

During interdiffusion between the solid metal (A) and the liquid metal (B), when in the A-B system several chemical compounds are present, the system after cooling, should be in a state of metastable equilibrium. The solidified part of the alloy, where the high-melting metal is dissolved, should correspond to the stable equilibrium phase enriched with the low-melting metal. But this part will not be in a stable equilibrium with the high-melting metal, since between them the continuous and mutual transition of the constituents A and B is interrupted.

As a result of interdiffusion of the constituents A and B through that layer of the joint, most rich in low-melting constituents, new layers are formed which, together with the precedent, constitute a continuous series of alloys in accordance with the equilibrium diagram. So, for instance, after diffusion of copper into molten zinc, between the copper layers and the ϵ -phase, layers of β and γ -phases are further generated.

Formation of chemical compounds during interdiffusion between high-melting and low-melting metals has been the subject of detailed studies, particularly in the case of soldering tin solders to copper or brass.

When copper or brass parts are soldered with tin or Sn-Pb solders, an interlayer of a non-etched intermetallic compound forms, always parallel to the alloy to be soldered. According to some authorities, this interlayer corresponds to the η -phase (Cu_6Sn_5); others on the contrary say that it corresponds to the ϵ -phase (Cu_3Sn). This vagueness inspired the authors of the present text to study the structure of the intermetallic layers in the soldered seam. In tin-soldered copper joints intermetallic compounds have been found both in the copper base metal and in the soldered seam (Figure 26).

The white non-etched intermetallic compound was separated from the solder after dissolution of tin in concentrated hydrochloric acid. The layer close to the copper base was detached by means of a file. X-ray examination of the cuttings and study of the undissolved precipitate by the powder method,

revealed a structure inherent also to the η -phase (Cu_6Sn_5).

Based on these data, formation of the η -phase when soldering tin to copper parts may be conceived as follows. Copper is dissolved in tin and causes formation of a liquid solution which is richer near the copper layer. During cooling, the η -phase crystallizes according to the equilibrium diagram. Copper (or the solid solution of tin in copper) acts as a wall on which nuclei of the η -phase are set up and continue to grow. Formation of the η -phase, due to the reaction-diffusion seems to be unlikely; also unlikely seems to be the separation of this phase in the molten solder (tin) owing to the diffusion of copper through this phase into tin; the crystals of the phase appeared during the process of crystallization of the liquid solution.



Figure 28. Microstructure of a copper joint soldered with tin solders after trial heating to 200°C for three weeks



Figure 29. Microstructure of a St-2 steel joint soldered with tin solders $\times 175$

The same intermetallic compounds appear also in soldering copper parts with solders on a Pb-Sn-Sb base, but in this case the layer thickness is smaller.

Owing to the nonequilibrium state of the η -phase on the border with the copper layer, subsequent heating of the soldered joint leads to creation of a single layer which corresponds to the δ -phase (adjoining the copper layer) and to the η -phase (Figure 28); the η -phase is brittle and therefore, as a rule, failure of the soldered joint during rupture testing may occur in this layer.

During soldering steel parts with tin-base solders chemical compounds FeSn_2 (white phase) are also formed (Figure 29).

Silver solders and silver-rich alloys used in steel soldering as well as cadmium and cadmium-rich solders required for soldering steel and aluminum parts, do not form with the base metal visible solutions in the liquid and the solid state.

Polished microsections of joints soldered with similar solders reveal no visible dissolution of the base metal or traces of diffusion of the solder into the solid base metal. The edges of the soldered parts appear with all their irregularities formed during polishing of the microsection (Figure 30).

It would be erroneous, however, to say that in this particular case a diffusion process leading to a rigid bond did not occur. According to exact investigations, cadmium and silver are partially dissolved in iron. The high rate of inter-diffusion between the constituents, associated with a reduced mutual solubility, permits us to draw the conclusion that in this particular case of soldering, the intensity of the diffusion process is not too high but nevertheless sufficient to insure the requisite coherence between the solder and the base metal.

This assumption is confirmed by the fact noticed in soldering 1Kh18N9T stainless steel with PSr40 solders: as it was found, during high-frequency induction soldering, the momentary contact of the base metal with the molten solder after its penetration into the gap between the parts, is not sufficient to insure a rigid bond between the parts involved. After feeding of the molten solder into the gap, a minimum contact time of two minutes between the molten solder and the base metal is necessary to achieve diffusion and to assure a rigid soldered joint.



Figure 30. Microstructure of chromium-molybdenum steels soldered with MSr-40 silver solders (in the seam the eutectic structure of the solder can be recognized) $\times 450$

It should be emphasized that the solders used in these investigations have not been in a spectrally pure form; they contained impurities which essentially affected the development of the processes involved. So, for instance, aluminum forms no visible solid solutions or chemical compounds with cadmium, but in soldering aluminum with commercial impure cadmium solders, a two-phase layer between the solder and the base metal is formed.

§ 5. The Process of Eutectic Crystallization During Soldering

Eutectic crystallization during soldering can be encountered in three instances of soldering: 1) soldering with eutectic solders; 2) soldering with solders which, though not eutectics, form (in the liquid condition) a eutectic with the base metal or alloy; 3) when a soldered joint results from the so called contact melting of the metals involved, between which a eutectic may be formed.

In view of the great importance of the eutectic crystallization during soldering, a brief examination of the peculiarities of the eutectic structures may be useful /30/-/32/.

A eutectic may be defined as the lowest melting alloy composed of constituents with a limited mutual solubility. It differs from a chemical compound by the presence of multiphases and the absence of stoichiometric proportions between its constituents.

From pure mechanically formed additive mixtures, the eutectic differs in its constant and minimum melting-point as compared with alloys of a nearly similar composition.

As shown by Bochvar /33/, the process of crystallization of binary eutectic alloys essentially differs from the crystallization of other kinds of alloys.

At a great cooling rate on the place where the crystals of two phases come in contact, the so called columnar eutectics develop which are typical of many metals. When eutectic columns are formed, one of the phases first crystallizes, being the so called "guiding" phase, whereas the other phase (the "guided" phase) grows next.

On polished microsections the eutectic column consists of alternating lamellas or of concentrically elongated (stretched) or punctiform inclusions of one phase in the other (Figure 31).

In metallic alloys of eutectic structure, the eutectic usually crystallizes in a columnar shape even at very slow rates of cooling. The conglomerate structure of pure eutectic alloys so far has been noticed only in alloys of organic matter and in rocks of volcanic origin, (the so called pegmatites).

A conglomerate eutectic structure in binary metallic alloys occurs only at a relatively reduced amount of their eutectic and if the latter forms very thin interlayers on the grain boundaries of the solid solution. This form of a eutectic structure is termed eutectoid and is essentially a variety of the conglomerate structure (Figure 32).

At a very high rate of cooling, eutectic spherulites can be observed, as, for instance, in the structure of very fast-cooled, gray, cast-iron.

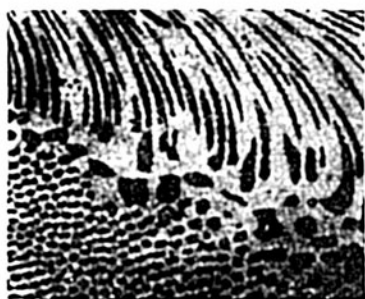


Figure 31. Microstructure of an Ag-Cu eutectic $\times 200$



Figure 32. Microstructure of a eutectic in a D-16 alloy joint soldered with a V61 solder $\times 350$

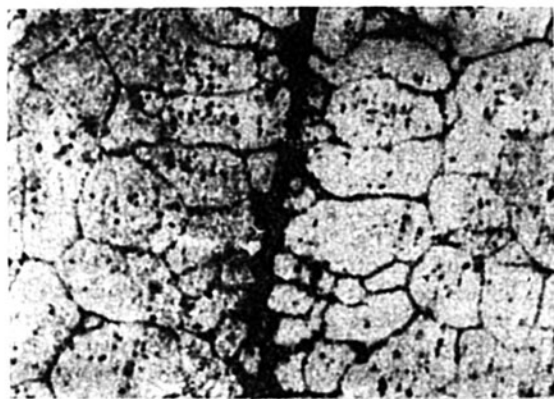


Figure 33. Microstructure of a nickel-alloy joint soldered with a Ni-B base solder $\times 300$

Among the soldering alloys, all the previously described types of structure may be found. Many commercial grades of eutectic solders have

a columnar eutectic structure. Such are e.g. the binary eutectic alloys on the base of Cu-P, Ag-Pb, Ag-Cu, Al-Si, Pb-Sn, etc.

Other types of eutectic structures can be encountered among commercial solders which, apart from the eutectic, include in their structure also an excedentary phase.

The influence of a eutectic solder on the soldered base metal is particularly strong when one of the phases of the eutectic constitutes at the same time the basic phase of the metal to be joined. In this case, the molten solder penetrates along the grain boundaries of the base metal, forming there a eutectic inter-layer. Among such solders are the above stated Ni-B eutectics which, during soldering of nickel alloys, form along the grain boundaries a branched (ramified) eutectic interlayer (Figure 33). This interlayer appears as a result of the reaction-diffusion process of the second order.

Such a formation of a eutectic structure takes place when metals or alloys, which are liable to form eutectics with the soldering alloy, are soldered. This may be illustrated by the example of soldering tin to a zinc base-metal. Zinc (9% Zn) forms with tin a simple eutectic which melts at 199°C. Mutual solubility of zinc and tin so far could not be revealed but it is known that the solubility of tin in zinc is very low.

Liquid solder-tin (Figure 34) penetrates along the grain boundaries of the soldered seam. The process of diffusion of tin into zinc may be explained in the following manner.



Figure 34. Microstructure of a tin-soldered zinc joint; the seam possesses a microdispersed Zn-Sn eutectic X300

Due to interaction of molten tin with zinc, a eutectic is formed. Such an interaction takes place most intensively along the boundaries of the grains as a result of the peculiar energetic state of the latter (the weakest chemical bond); this in turn leads to formation of a peculiar eutectoid structure in which tin can be found along the grain boundaries.

This form of eutectic is also called eutectoid.

As shown on Figure 34, the molten tin seems to wash off the zinc grains on their boundaries; they pass into the solder in the form of undissolved residues.

The diffusion of molten bismuth into copper and of molten sulphurous nickel along the boundaries of the nickel grains is undoubtedly a result of the reaction-diffusion process of the second order, since copper and bismuth as well as sulphurous and pure nickel form pairs of eutectic structure.

Diffusion of a molten metal along the grain boundaries of another metal has various causes. One of them is the formation of a eutectic structure. Another reason may be the formation of a peritectic. The penetration of molten copper along the grain boundaries of steel at a temperature, higher than the melting point of steel is not a simple physical process but is doubtless connected with the apparition of a peritectic structure.

In some cases the molten metal may penetrate along the grain boundaries of the solid metal. This phenomenon is a process of pure physical diffusion and occurs most frequently when the metal is subjected to tensile stresses.

Penetration of a molten metal along the grain boundaries of another metal may occur also as a result of the interaction of the metal with gases.

Instances of penetration of molten copper along the grain boundaries of steel due to the reduction of copper oxides are quite frequent /34/.

Formation of eutectic structures during the contact-melting soldering process will be discussed in more details later in this text when the contact melting process will be given an ample consideration.

§ 6. Influence of Gases on the Soldering Process and on the Quality of the Soldered Seam

Gases drawn from the environment into the liquid or solid metal or during pickling or electrolytic machining cause, under certain conditions, profound changes in the properties of the metal involved. Hydrogen has a particularly great influence on the properties of metals or alloys. The action of hydrogen on the metal's properties may be explained by the change in the solubility of hydrogen at different temperatures and conditions of the metal and by its transition into the alloy or metal from the atomic to the molecular state. The hydrogen atoms, diffusing into the metal or alloy are filling its cavities, e.g. shrinkage holes (the so called "voids") where they form hydrogen molecules, practically insoluble in metals. Cooling of plastically deformed steels is associated with a sudden change in the solubility of hydrogen; accumulation of the latter leads to formation of flakes (more frequently on the slip planes in the structure) /35/. The molecular hydrogen accumulated in the heated metal, suffers an intensive expansion; the hydrogen tends to move from the metal preferring the less compact (dense) parts of the metal, and leads sometimes to local failures. Rapid heating of the parts to be soldered (which are) saturated with hydrogen, may cause destructions along the grain boundaries. Such a phenomenon is observed during dip soldering of hydrogen-bearing steel with brass solders. The molecular hydrogen in the steel parts immersed in molten brass, moves along the grain boundaries and causes loosening (widening) of the structure. In the so widened boundaries, liquid brass penetrates. Sometimes when steel parts are soldered with brass solders, a destruction along the grain boundaries close to the soldered seam can be noticed. The destruction is developing

along the same grain boundaries which have been previously loosened by the hydrogen during soldering.

In cold deformed metal the molten solder exhibits a preferential (selective) penetration along the grain boundaries, a fact which may be noticed in soldering of various alloys; sometimes this is connected with the influence of gases which assist the loosening (widening) of the grain boundaries.

Hydrogen, penetrating in some alloys or metals forms, under certain conditions, volatile compounds which cause local failures or gas bubbles (blow holes). This can be noticed when copper, containing cuprous inclusions is heated (particularly for soldering purposes) in a hydrogen atmosphere. Hydrogen after diffusion into copper, reduces the cuprous oxide and forms water vapors leading to the so called hydrogen embrittlement.

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Chapter IV

DESTRUCTIVE EFFECTS OF MOLTEN SOLDERS ON SOLDERED PARTS DURING OR AFTER THEIR SOLDERING

Instances of spontaneous local failure of parts during or after their soldering as a result of repeated melting of the solder on the places of tinning /1-18/ have been known for a long time. Such failures have always been noticed in places subjected to tensile stresses, concurrently wetted by liquid solder. The causes of the tensile stresses have been various: applied external forces; rigid jiggling of the parts during or after their soldering; sudden heating of the parts leading to a non-homogeneous field of tension; plastic deformation. On the other hand, spontaneous cracks did not appear in soldered joints where the tensile stresses were previously relieved (removed). As a rule, cracks in soldered joints caused by molten solder occurred without visible plastic deformation. This type of failure should be distinguished from failure of soldered joints without melting of the solder, as a result of reduced mechanical strength or of low plasticity of the soldered seam.

Failure of solid metals under the action of liquid metals may occur not only during the soldering or in the soldered joint but generally under the wetting action of liquid metals on metallic parts subjected to tensile stresses.

In the following, some instances of spontaneous failure of metallic parts under the effect of liquid alloys or metals may be considered.

Axles of railroad cars or of various engines are destroyed under the effect of the molten lining of their bronze bearings /4/, /10/. The molten bronze is drawn in along the grain boundaries of the stressed metal and weakens the metallic bond of the structure. In some cases, penetration of the molten metal into the cracks is not the cause but the result of a destruction process: the molten metal flows into the cracks formed during the destruction.

In order to prevent vibrations of chromium and chrome-nickel steel turbine blades, a wire bandage is soldered onto them. A careful study of the cases of failure of the blades revealed that the cracks appearing during soldering with silver solders, were filled with molten solder /4/, /16/. In turbine blades, cracks appear most frequently due to a sudden torch-flame heating (for soldering purposes) which leads to formation of thermal stresses. Slow heating of the blades does not cause such cracks.

In spherical or hemispherical steel parts subjected to stresses, cracks may sometimes appear during soldering with tin-lead solders. So, for instance, in soldering such parts, cracks appeared in the indentations caused by shocks /14/.

Such failure may occur when soldered parts, before their subsequent tightening are heated above the melting point of the solder.

When nipples are soldered to Kh18N9T steel tubes with brass solders by heating in a gas flame or in an induction furnace, the tubes exhibit a tendency to brittle fracture under the action of tensile and bend stresses set up in them. Usually, destruction develops in the soldered seam or in the zone of thermal influence of the soldering process along the cracks formed during soldering. Formation of cracks is fostered by the penetration of molten brass along the grain boundaries. Fine (hair) cracks and indentations on tube walls also may be a source of cracks during soldering.

Formation of cracks during soldering of tubes can be avoided by suitable methods of thermal-stress relieving (furnace brazing, dip soldering, etc), by annealing or by applying silver solders which apparently do not penetrate along the grain boundaries of the steel.

Cracks may sometimes appear when molten tin-lead solders come in contact with places of steel parts, previously subjected to marking operations.

In certain cases spontaneous or premature destruction of tin-plated or cadmium-plated stainless 30KhGSA steel parts occurs after their heat treatment (quenching from 880°C and annealing). The study of these cases of destructions revealed that during the heat treatment of steel parts the molten metals (tin or cadmium) cause local destruction of the parts. In this case, intercrystalline penetration of the molten metals could not be noticed.

In the manufacture of non heat-treated parts, tin-plated with low-melting metals, spontaneous or premature destruction could not be noticed.

Most of the cases of spontaneous destruction were accompanied by penetration of the molten metal along the grain boundaries. Therefore, some researchers considered this type of destruction as an intercrystalline phenomenon, though destructions occurred without even a visible penetration of the molten metal along the grain boundaries.

Most responsive to such a type of destruction are soldered parts of stainless chromium-steel of nichrome or of monel metals (nickel-copper alloys). These alloys have a low thermal conductivity, and therefore, under the action of non-uniform heating, thermal stresses are quite easily set up assisting the action of molten solders.

Cold hardened alloys are particularly prone to such cracks. Metallic parts, when subjected to the action of molten solder during tinning or dip soldering, show less tendency to non-destructive plastic deformations than parts plastically deformed in an atmospheric environment. This is confirmed by the following. Stainless 1Kh19N8T steel tubes, 10 mm in diameter and 1 mm in wall thickness, heated up to 906°C and tinned with various solders, when subjected to bending stresses, attained the following maximum angles of bend: 7°, with L62 solders; 26°, with PSr40 solders; 32°, with solders containing 65% Ag, 28% Cu, 2% Ni and 5% Mn; and 90° when bent without solders.

Liquid media exert a strong influence on metals or alloys subjected to a tensile or bending test (whereby the fibers are elongated) but have no influence or a reduced influence on parts stressed in compression.

Certain aluminum alloys, when in a state of tension, are subjected to spontaneous destruction during soldering with tin or with solders containing 90% Sn and 10% Zn. Among such responsive (sensitive) alloys are the heat-treated alloys of the ternary Al-Mg-Si, Al-Mg-Zn, system and the alloys of the binary Al-Mg system (subjected to a large preliminary deformation). Al-Mn alloys, (annealed and cold hardened) as well as annealed ternary Al-Mg-Si alloys, when in a state of tension, are not subjected to destruction during soldering. Thanks to the use of tin-base solders with a melting point higher than the annealing temperature of aluminum alloys, formation of cracks during soldering or tinning can be avoided /9/.

Such pure, plastically easy deformable metals with a face-centered crystalline structure (lattice), as copper, nickel or certain aluminum alloys (AMts and duralumin), when tensile tested in liquid tin-lead solders and (concurrently heated up to 270-300°C), are destroyed with a visible plastic deformation. In this case, changes in the mechanical properties of copper and nickel are smaller than in the case of tensile testing in an atmospheric or oil environment. Aluminum, AMts alloys and duralumin specimens, when tensile tested in liquid solders exhibit a smaller tensile strength but a greater area reduction than in the usual tensile test /7/. This may be attributed to the fact that molten tin, inter-acting with the tensile specimen, partially dissolves aluminum or its alloys, thus hindering the development of a common elongation and causing local deformations. Owing to the insensibility of aluminum to notches, the specimens, if under a prolonged load, continue to be plastically deformed until they reach a large area-reduction.

It should be emphasized that investigations of the influence of molten solder on the mechanical properties of metals and alloys led to inexact conclusions /12/, /14/. So, for instance, in tinning certain metals or alloys with tin-containing solders, a flux was used composed of a saturated solution of zinc chloride. Soldering of certain alloys (particularly on an aluminum base) with zinc chloride fluxes is associated with the reduction of zinc from the flux, the zinc being drawn into the solder.

According to some authors, the influence of liquid lead on steel is chiefly due to the state of purity of lead /14/, despite the known fact that pure lead has a poor wetting action on steel. These authors overlooked the fact that zinc, reduced from the flux takes part in the soldering process (molten zinc has an active influence on steel during soldering), as well as the fact that the probable presence of impurities (even in insignificant quantities) has an essential effect on the diffusion into the base metal. In some studies on the influence of molten solders on high-alloyed chromium steels /11/, fluxes were described which do not remove the oxide films from the surface of the base metal before and after the tinning operation.

As shown by the authors of the present study, tinning of pure (99.99%) aluminum specimens with ternary eutectic Al-Cu-Si (34A) solders, melted for five minutes at 525 and 610°C, caused a visible embrittlement of the test specimen (as compared with non-tinned specimens). The higher the temperature of the testing, the stronger the action of the molten solder which in the course of tensile testing, dissolves aluminum and causes its premature destruction.

According to available information, molten media chemically inter-acting (wetting) during tensile or bend testing with the tested metals or alloys, exert a definite influence on the mechanical characteristics of the latter.

In many cases, the mechanical properties of tinned specimens tested at room temperature differ only little or not at all from the properties of non-tinned test-specimens.

The strongest interaction of liquid metals with deformable solid metals occurs in the case of an uninterrupted contact between them. Any interruption of this contact reduces the influence of the liquid medium. This can clearly be seen when tinned specimens are tested having different rates of deformation (with a more or lesser rate of penetration of the molten solder into the nascent cracks). Table 5 presents data on the testing of 1Kh18N9T steel specimens, tinned at 950°C with an L62 solder and a No 201 flux.

Table 5
The effect of the rate of deformation on the mechanical properties of 1Kh18N9T steel, tinned and not tinned with L62 brass (according to Gubin)

Rate of deformation, mm/min	Test temperature °C	Tinned specimens			Non-tinned specimens		
		Tensile strength, σ_v kg/mm ²	Elongation, δ %	Reduction of area, ψ %	Tensile strength, σ_v kg/mm ²	Elongation, δ %	Reduction of area, ψ %
6120	925	21.0	29.3	28.4	20.8	20.8	20.1
	950	20.1	31.1	28.4	20.6	27.3	20.0
	1000	18.6	36.6	38.1	17.3	35.0	29.7
75	925	15.4	51.6	69.4	13.6	0	0
	950	14.2	51.7	67.3	13.3	0	0
	1000	10.2	56.4	67.6	8.2	0	0
0.07	925	10.3	50.3	62.8	9.4	0	0
	950	8.2	51.3	69.4	7.7	0	0
	1000	6.4	58.4	79.0	5.0	0	0

The increase in tensile stresses has the same effect as the increase in the temperature of the molten metal /11/-/14/.

Steels or alloys with a non-equilibrium structure are more responsive to the action of liquid solders during tensile stresses than equilibrium alloys. This is true for martensitic steels subjected to annealing (see Table 6).

The cadmium-coated EI437B alloy lowers its mechanical strength in the course of tensile testing at 400-500°C and becomes brittle. The tensile strength of non coated EI437B alloys equals 98-102 kg/mm², but lowers after coating with cadmium to 30 and 16 kg/mm² respectively; the elongation drops also from 23 to 0%.

After oil quenching from 880°C and annealing at 300°C, the tensile strength of a 30KhGSA steel specimen is 170 kg/mm²; after quenching and annealing at 500°C, the tensile strength is only 120 kg/mm²; after annealing at 670°C, the tensile strength is also 75 kg/mm².

Molten lead-solders with a high tin content have a stronger action on steel and copper alloys submitted to tensile testing, than solders with a

smaller tin content, i.e. their action depends upon the ability to interact chemically with the tested alloy. Molten tin has a greater dissolving effect on copper and iron than lead.

According to Goodrich /6/, the effect of molten tin solders on the mechanical properties of steel, increases with the increase in the size of the metallic grains.

The effect of molten metals on alloys depends on the solubility of the metals or alloying elements in the molten metal. So, for instance, nickel is more soluble in lead than cobalt; chromium and iron are less soluble /19/. Molten lead in which nickel-bearing steel has been immersed, dissolved first the portions of the grain or phase, which are most rich in nickel; e.g. in austenitic steel containing 19% Cr and 9% Ni, the grain boundaries more rich in austenite are faster dissolved; in molten lead in which a 47% Fe, 37% Cr and 16% Ni steel composed of an austenitic and σ -phase has previously been dissolved, the Ni-rich austenite is faster dissolved than the σ -phase which has a smaller Ni-content. Chromium stainless steels without any Ni-content are more resistant in molten lead than nickel-rich steels. This applies also for steels immersed in low-melting bismuth alloys (55.5% Bi and 44.5% Pb; 52% Bi, 32% Pb and 16% Sn; 52.3 % Bi, 25.8 % Pb and 21.9 % In) /20/.

Embrittlement of a tinned alloy can often be noticed at a temperature higher than the melting point of the solder; this is associated with a general diffusion of the solder into the uniformly dissolved alloy. This fact may be observed, particularly in testing tinned heat-resistant EI437 steel specimens at 300°C.

Liquid metals, while in contact with solid alloys, affect not only the mechanical properties obtained during a short tensile or bend test, but even those which result after endurance and fatigue testing. The endurance limit of mild steel stressed in tension and compression while immersed in molten tin at 300°C, is 2 kg/mm² smaller than when tested in open air.



Figure 35. General view of an armco brass-welded ring and rod; as can be seen, the portions of molten brass which penetrated from the soldered seam into the ring are radially disposed (spread). $\times 1$

Molten tin /12/ has a great influence on the reduction of the endurance limit of EI437 steel; molten zinc, at a range from 425 to 500°C, affects

the endurance limit of plain steel /18/ etc.; it penetrates along the grain boundaries of the latter.

Table 6

Influence of the structure and testing temperature on the mechanical properties of tinned alloys /12, 14/

Grade of material	Solder	Test temperature, °C	Tinned specimens			Non-tinned specimens		
			Tensile strength, σ_v kg/mm ²	Elongation, δ %	Area reduction, ψ %	Tensile strength, σ_v kg/mm ²	Elongation, δ %	Area reduction, ψ %
30 KhGSA steel	Tin	270-280	115.2	1.5	2.0	165.9	13.3	58.3
$\sigma_v = 170$ kg/mm ²	"	270-280	96.2	2.7	7.9	121	10.7	52.0
Idem,	"	400	22	0	0	105	13.2	36.7
$\sigma_v = 120$ kg/mm ²	"	500	25.2	0	0	86.0	14.8	77.8
Idem,	"	270	75.5	20.0	66.3	74.0	21.2	67.3
$\sigma_v = 75$ kg/mm ²	"	400	68.7	6.4	11.0	70.5	22.7	69.0
	"	500	46.0	2.0	6.0	59.8	19.1	72.0
Austenitic	"	270	73.3	33.3	50.5	70.4	30.8	54.3
EI388 steel	"	400	66.5	26.0	29.2	72.0	33.5	51.0
	"	500	58.5	18.8	24.1	71.5	38.0	38.2
LS 59 brass	"	270	29.5	7.7	17.4	40.3	17.5	27.7
EI437 steel (after quenching from 1080° and aging at 700° for 30 hours)	POS-61	280	98	—	12.6	112.5	—	34.9

In wetting stressed solid alloys, liquid metals have a preferential action not only on the grain boundaries, but even on the structural components. Molten solders, penetrating into α - and β -brasses dissolve first the grain boundaries, whereas in the two-phase brasses, the β -phase is preferentially dissolved /21/.

Sometimes, the embrittling action of molten solders on alloys can easily be detected when subjecting to bending test, alloy lamellae at a temperature higher than the melting point of the solder applied on the lamellae. So, for instance, copper specimens when bend tested, exhibit no intercrystalline destruction in the presence of molten silver solders, whereas iron-alloyed monel metals containing 10-30% Cu, are subjected, under the effect of these solders, to intercrystalline destruction /22/.

Cold hardened or deformed monel metals suffer an intercrystalline destruction only in molten silver solders but not in liquid brass solders. This may evidently be explained by the different solubility of the center and the boundaries of the monel grains in silver solders.

Figure 35 illustrates the effect of tensile deformations set-up in a ring

on the penetration of molten solder into the parts to be soldered. In manufacturing a magnet yoke, an armco-iron ring has been soldered to a rod of the same alloy, by means of an L62 brass-solder. Due to the large gap (4 mm), no capillary soldering has been applied but braze welding. Under the effect of heating prior to soldering, the ring suffered a larger expansion than the rod; upon cooling of the hardening solder, the ring is subjected to tensile stresses, while the rod to compressive stresses. As a rule, the grain boundaries of armco-iron are weakened by oxides or low-melting components (sulphides etc). Deformation of the armco-iron in the region of the polymorphic $\gamma \rightleftharpoons \alpha$ transformations causes brittle failure (fracture).



Figure 36. Microstructure of the metallic ring shown in Figure 35, at the place of inflow of molten brass $\times 350$

Tensile stresses in the armco-iron ring cause along the grain boundaries numerous radial cracks filled with molten brass (Figure 36). In the compression-stressed rod such cracks could not be noticed.

The previously described facts of the embrittling effect of molten solders on the base metal (alloy) subjected to tensile stresses are revealed when:

1. Molten metal wets the alloy; wetting of the solid metal by liquid metals may occur when solid solutions or chemical compounds (including eutectics) are formed between them.

2. Tensile stresses are present in the alloy subjected to the action of molten solders.

In order to explain the destructive effect of molten solders on stressed base metals, the following theories have been advanced:

1. When a solid metal (or alloy) is wetted by liquid metals (or alloys), its surface energy is diminished causing reduction of the resistance to rupture and to brittle failure.

2. Liquid metals form with the solid metal, alloys which possess a smaller resistance to brittle failure.

3. Molten metals are surface active media; being absorbed on the surface of a solid metal, they penetrate into the previously formed cracks and cause their widening (the so-called Rebinder effect).

4. The effect of molten metals on solid stressed alloys or metals is similar to the effect of a corrosive medium (agent) on a stressed body. This effect is actually a variety of the stress-corrosion effect [23/.

The first hypothesis of the reduction of the surface energy has no concrete support. The second hypothesis gives no satisfactory explanation of this phenomenon, since the latter may occur without a visible alloying of the solid alloy with the components from the molten metal (e.g. the effect of molten commercial lead on steel). The third hypothesis does not take into account the invariable dissolution of the solid alloys in the molten one. As shown by Austin, the presence of a medium (e.g. an oil bath), which wets the solid alloy, without dissolving it, is not sufficient to cause its embrittlement during deformation. Though a widening effect of the wetting molten metal seems to take place, no detailed figures are available which could actually permit us to estimate the resistance to failure. The fourth and last hypothesis affords the most judicious explanation of the phenomena encountered during the investigation of the effect of molten metals on stressed parts.

Failure of stressed metals or alloys under the action of corrosion, occurs almost in the same way as destruction of stressed parts by molten metals.

Usually, under the effect of corrosion, destruction of stressed parts occurs in the anodic portions of the metal. In certain stressed metals, such portions are the grain boundaries; along them the phases, most actively soluble in liquid media are first separated as well as the most stressed portions, especially the places of slip planes in the structure of cold-hardened metals. The anodic portions of metals are locally dissolved in these places and peculiar sharp notches are formed which accelerate the process of destruction of the stressed parts.

Corrosion of stressed parts differs from the action of molten metals on stressed alloys in the mechanism of the primary damage caused to the alloy. During corrosion of stressed parts, in the first place the stressed anodic portions of the galvanic cells (couples) are preferentially dissolved, whereas the brittle fracture of stressed alloys is apparently connected with a local chemical dissolution of the alloys in the molten metal. Like any diffusion processes, dissolution occurs more rapidly in the most stressed portions of the alloy and in those portions which are in a non-equilibrium state or at elevated temperatures.

The particular condition of the alloys on the grain boundaries, where the junction of differently oriented crystalline lattices induces in the metal a stressed state, favors in many alloys a local dissolution in molten solders, which leads to embrittlement of the whole alloy during its deformation. If the molten solder or its components form a eutectic with the base alloy, the grain boundaries will be the most favorable medium for the development of a reaction-diffusion of the second order [24]. Along the grain boundaries a eutectic is formed which often has an embrittling effect on the alloy, weakening the binding along the grain boundaries. The grain boundaries of many alloys are enriched with certain alloying elements. In brasses, the grain boundaries are enriched with zinc; at the grain boundaries of some alloys a larger concentration of nickel has been noticed than within the grains themselves, etc. Such a non-uniform distribution of the alloying constituents in the grains promotes in certain cases the preferential dissolution of the grain boundaries in molten solders or generally in lower-melting alloys.

In order to avoid spontaneous failure of soldered or tinned parts after their repeated contact with molten solder and destructions connected with the appearance of fine cracks during the soldering process, the sources of macro and micro tensile stresses in the soldered parts should be removed; the removal of macrostresses may be achieved by:

1. by stress-relieving of the cold-worked metal through annealing;
2. by reduction of the rigidity of the joint;
3. by slow heating which prevents the possible appearance of thermal stresses; by using soldering methods which do not generate thermal stresses (furnace or dip soldering);
4. by pre-heating the parts to be joined above the temperature of stress-relieving, followed by cooling down to the soldering temperature.

Microstresses causing sensitivity to stress corrosion may appear also as a result of non-equilibrated processes, which are connected e.g. with the following structural transformations:

1. Polymorphic transformations of a martensitic type, when, as a result of cooling, a modified non-equilibrium, low-temperature phase is created, between the different blocks (most frequently of a laminar or acicular form) in which elastic stresses are set up.
2. Decomposition of the supersaturated solid solution, associated with a separation of phases of another specific volume than of the non-saturated solution, which leads to appearance of elastic microstresses between the two phases.

By bringing the alloy to a state of equilibrium, the primary sources of structural microstresses may be removed.

It seems feasible to avoid brittle fracture by preliminary coating of the parts to be soldered, with metals not subjected to brittle failure when applied together with molten solders.

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Section Three

SOLDERS AND FLUXES

Chapter V

SOLDERS PREPARED OF VARIOUS BASE METALS

The growing technical expansion led to the widening of the assortment of the parts joined by soldering, and also of the soldering alloys involved. Selection of a corresponding soldering alloy with prescribed properties is dependent on the requirements the soldered joint has to meet with.

The most important characteristic feature of a solder is its crystallization range which is limited by the temperature of the solidus and liquidus. The soldering temperature depends on the temperature of the incipient coherence between the dendrites growing from the primary phase of the solder during its crystallization.

Generally the soldering temperature is determined by the temperature of the liquidus. This means that a large assortment of solders with various temperatures of the liquidus and solidus should be commercially available.

For the time being, solders with a melting point below zero are not in use though they may be used at low temperature. To such low-melting alloys belong the Hg-Bi eutectics with 0.1 % Bi having a melting point of minus 39.2° C (mercury melts at minus 38.87° C). Certain gallium and indium alloys have the melting point below 30° C. These alloys will probably be used as solders (see table 7).

Gallium melts at 29.8° C. The melting point of many soldering alloys with a high bismuth content ranges between the melting point of gallium and that of the known quinary Bi-Cd-Pb-Sn-In eutectic (46.7° C).

Bismuth solders cover the crystallization range from 41 to 145° C.

Different eutectics with a Sn, Pb, Cd or Ti content (Table 8) cover the melting range from 145 to 183° C (the latter being the melting point of the eutectic solder with 62.3 % Sn and 37.7 % Pb).

Many binary or ternary alloys of the Sn-Pb or Sn-Pb-Sb (0.5-3.0 % of Sb) system used as soldering alloys, cover the melting range from 183 to 250° C. A long time the melting range from 250 to 860° C remained unknown. The use of alloys on a lead-silver-base (Pb-Ag) and on a cadmium base permitted us to widen the range from 250 to 420° C.

Thanks to the use of zinc, soldering alloys with a melting range from 380 to 500° C could be prepared.

Aluminum-base solders have a melting point which ranges from 470 to 600° C. The melting point of quaternary alloys on a silver base ranges from 600 to 780° C and from 960 to 980° C. (Ag-Mn alloys).

Addition of copper permitted us to use solders with a melting point ranging from 625° C (in the case of the ternary Cu-Ag-P eutectic) to 1200° C

(alloys with a considerable amount of elements from the transitional group: iron, nickel or manganese). The melting point of pure copper is also covered by this range (1083°C).

Table 7

Eutectic alloys with a melting point below 30°C

Composition of eutectics					Melting point in °C
Ga	In	Sn	Zn	Tl	
61	25	13	1	-	3
62	25	13	-	-	5
67	29	-	4	-	13
76	24	-	-	-	16
82	-	12	6	-	17
92	-	8	-	-	20
95	-	-	-	-	25
99.5	-	-	-	0.5	27.3

Table 8

Eutectic alloys with a melting range from 145 to 183°C

Composition of eutectic, %				Melting point in °C	Composition of eutectic, %				Melting point in °C
Cd	Pb	Sn	Tl		Cd	Pb	Sn	Tl	
18.2	32	49.8	-	145	32.25	-	67.75	-	176
31	66.5	2.5	-	163.6	-	24	71	5	177
-	-	57	43	170	-	37.7	62.3	-	183

The melting range of gold solders is close to the melting range of copper-base alloys.

The melting point of iron and nickel base solders containing low-melting eutectics, ranges from the melting point of the eutectics to that of metals in the pure form.

For the time being, solders having constituents with a higher melting point than Fe and Ni are of a limited use, but in the future, the melting point of such solders will undoubtedly exceed the limit of 1550°C.

At present, a great variety of solders has been suggested, described and given patent rights.

During World War I, the existing stock of tin could not satisfy the growing demand of various countries in tin solders; this led to the development of a tremendous number of substitute-soldering alloys.

In this section only those features of the solders are dealt with which

from the authors' point of view deserve more attention. Many solders seem to lose their individuality during the soldering process, being dissolved in the soldered seam. It must be stressed that in general the soldered seams have been characterized only from the point of view of their quality, the quantitative aspect of their properties being neglected. In soldering irregularly shaped parts a quantitative appreciation of the soldered joints is usually very difficult.

In the present section, only those solders are given consideration which are prepared on the basis of the most commonly used metals. Certain solders have been omitted since they are described later in the chapter on soldering of metals and alloys having various constituents.

The use of certain constituents in soldering alloys, most frequently metals in the pure form (e.g., Ta, Nb, etc) is so far rather limited; this refers also to solders prepared on a Pd or Pt-base, which are not included in a special group of solders.

Such a diversity of soldering alloys, of their use and properties could not but lead to a variety in their shape and in the method of production. Solders are made either by deformation or by casting, in dependence on their deformability, their methods and economy of production and finally on the suitability of their shape. Soldering alloys are available in the form of foils, wire, stripes, pieces or dispersed grains, shot or powder. Their composition may be homogeneous but they are available also in a heterogeneous form, e.g., as composite or pasty solders or mixed with fluxes etc.

Homogeneous solders are prepared either by casting or by deformation of precast soldering stocks.

The manufacture of soldering alloy requires certain skill and knowledge. The melting of a soldering alloy is done in furnaces with a special lining or in crucibles which do not chemically interact with the alloying elements; copper, aluminum and its alloys, for instance, may be molten in graphite crucibles, whereas for melting of iron and nickel alloys, graphite crucibles are not suitable. The form in which the components of the charge are put into the melting unit is also of paramount importance in a high-quality melting process: high-melting elements are put in the form of relatively low-melting intermediate alloys (e.g., copper is added to the aluminum solder in the form of an intermediate alloy with 50 % Al and 50 % Cu; silicon is added in the form of duralumin, etc).

Of importance is also the sequence of the charging of the alloying constituents into the melting furnace, which depends on the oxidability of the constituents, on their chemical interaction with other elements etc. As a rule, the less oxidable constituent of the solder is first molten (e.g. when manufacturing tin-lead solders, tin being less oxidable in the liquid condition, is first molten; the easy-oxidable lead is then added to the charge of molten tin). In order to prevent oxidation of the surface of the molten alloy, the latter is to be covered with a protective or low-reactive fluxing material or with slag which interacts with the molten bath (e.g., coal in melting copper or its alloys or tin solders; chlorides or fluorides, in melting aluminum or magnesium alloys, etc).

In order to remove from the metallic bath of the solder any traces of oxygen or other gases or non-metallic inclusions or in general other foreign matter, the method of deoxidation or refining with active agents is to be applied; these agents form with the impurities chemical compounds which

float on the surface of the molten metal and are then removed from it (e.g., phosphorus copper is used in melting of copper, etc).

The degree of dispersion of macro-and microstructure of the solder depends on the conditions of crystallization and the casting process, i.e., on the temperature of pouring and of the mold, on the rate of cooling and finally on the action of the special modifying additives (e.g., titanium in the aluminum alloys, etc).

Solders are cast into ingots, rods, shots or granulas. The molten solder is first poured into the ladle which is often of the more convenient tea kettle type. For casting rods of aluminum solder, a ladle of heat-resisting steel sheets 2-6 mm thick, is used (see Figure 37).

In accordance with the diameter of the ladle outlet d , the thickness of the soldering rods is as follows:

Diameter of the ladle outlet, mm	3	4	5
Thickness of the soldering rod, mm	4	6	8

Casting of solders is to be made on plain plates (of cast iron, steel or another material or on plates provided with grooves of a definite cross-section. Cast rods may be obtained also by pouring the metal in circular sand molds or in metallic molds or by drawing them through special tubes.

Brittle solders for soldering e.g., tubes of rectangular cross-section may be obtained by casting the molten solder into gratings which are then cut in separate pieces.

Powder-like solders are obtained from molten metal by atomizing, electrodepositing or by dry-grinding the metal in the crystallization range. Tin lead powder-solders are prepared by rubbing the alloy while in a solid-liquid condition, with special rags. The process of grinding the solder is speeded up by shaking the table on which the freezing mass of molten solder is located.

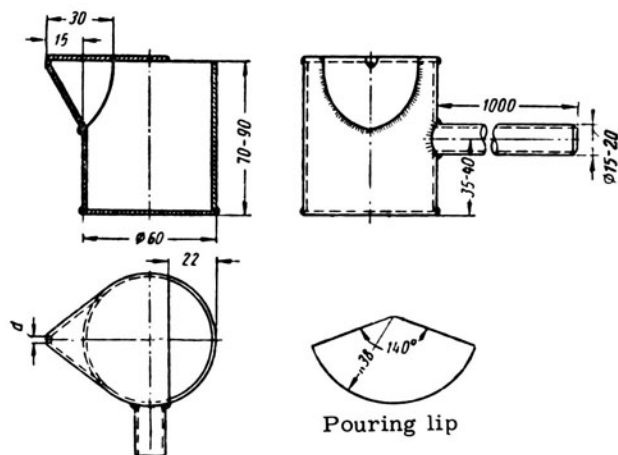


Figure 37. Sketch of the ladle for casting molten solders into rods

Shot-like solders are prepared by pouring the molten solder in water (the so-called granulation process). The size of the shot grains depends on the height of fall of the liquid metallic jet, on its cross-section, its temperature and on the turbulence of the water.

Powder solders may be obtained by grinding the alloy in special mills (particularly in ball mills); such procedure is most easily achievable with solders of sufficient brittleness.

Fine-grained solders may be obtained also by mechanical dividing of a partially crystallized alloy (while in a solid-liquid state) in rotating units, which are available in different constructions. Figure 38 shows a schematic representation of such a unit /1/.

Figure 39 schematically depicts an appliance devised by F.P. Frolov for preparing fine-grained solders. The molten solder is put into the casting ladle where it cools to a pasty state. After switching on the electromotor 1, the soldering mass, by means of a stainless steel paddle is fed into the drum 2, where it strikes the rotating blades 3, fixed on the axle 4; these blades crush the solder; the resulting grains are then picked up by the collector 5; during crushing of the solid-liquid mass of the solder by means of this appliance, on the surface of the grains the most fusible part of the alloy is hardened (solidified). Such a heterogeneous alloy melts faster than a homogeneous one. In order to promote the melting process of the solder, its surface is sometimes covered with a low-melting metal (e.g., brass is covered with tin, etc).

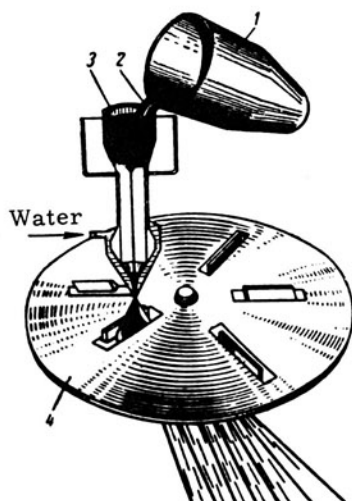


Figure 38. Schematic representation of a rotating unit for fabrication of granular solder in the crystallization range: 1. crucible; 2. molten solder; 3. receiving hopper; 4. rotation disk.

Thin foils of brittle solder may be produced by immersing in the molten solder a solid body which is not wetted by the latter. A non-wettable surface of the solid body may be assured by suitable coating, e.g., with a mixture of chalk and water glass (soluble glass), etc. After withdrawing the body from the molten solder the solidified solder remains on its surface in the form of a thin, easily removable layer.

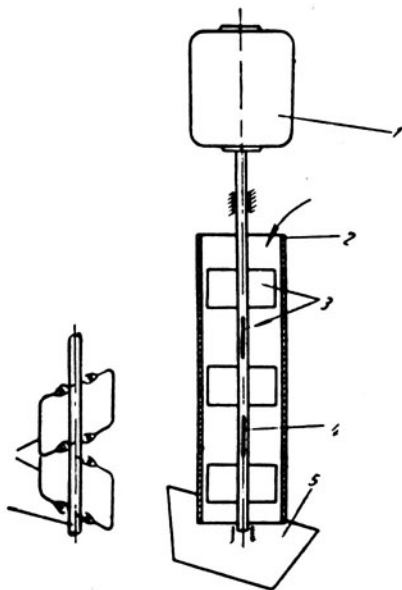


Figure 39. Schematic representation of the appliance for casting fine-grained solders

Solders irregular in shape may be obtained by machining. So, for instance, ring-shaped solders may be obtained from rods (sometimes of brittle alloys).

The melting rate of the solder and hence the rate of soldering depends on the ratio of the area of the particles to their volume. In case of a large total area, heating and melting of the solder proceeds faster than with a solder in the form of an isolated piece.



Figure 40. Various cross-sections of tubular solders

Wire, strip and thin foil-shaped solders may be obtained from plastically deformable solders by drawing, rolling or pressing. Strips are sometimes prepared from compact metal cuttings of a lathe. Such a procedure is suitable for the manufacture of strips from tin-lead laminated solders /2/ or from PFOTs-7-3-2 solders.

Heterogeneous solders are composite or compact. Heterogeneous compact-shaped solders are produced in the form of: 1) clad sheets (the so-called brazing sheets) where the clad layer constitutes the solder itself (e.g., aluminum alloys clad with silumin (alpac)); 2) multilayer sheets or rods, in which one of the layers in the initial period of soldering does not come in contact with the parts to be soldered or with the atmosphere (e.g., cored solders, whose core consists of a metal differing in its properties from the peripheral metal, etc).

Composite solders are prepared in the form of: 1) a paste consisting of mutually adhesive-bonded solder-grains; 2) a mixture of solder grains with flux; 3) soldering rods filled with flux /3/, /6/.

Mixtures of soldering grains with fluxes are particularly suited to soldering cutters on cutting tools.

Tubular tin-lead solders (of POS40, POS50 or POS61-alloys), filled with fluxes (e.g., with colophony powder of bright sorts) or with active fluxes, are most commonly used. Where tubular solders are required the solder and flux may be applied in a single operation. These solders permit soldering in places not easily accessible, their use reduces the losses in flux (by 50 %) and solder (by ~20 %) as compared with soldering by means of common solders or fluxes, and finally improves the quality of the soldered joints and the productivity.

Tubular solders may have various cross-sections. Initially, tubular solders were provided with circular cores. At present, tubular solders have shaped (profiled) cores or several longitudinal channels (see Figure 40) which ensure a more uniform feeding of both the solder and the flux.

The ratio of the amount of solder to that of the flux is of paramount importance for tubular solders. In electroinstallation soldering, satisfactory results have been achieved with tubular solders in which the amount of flux is 2-3 % of the total weight of the tubular solder. In tubular solders of a circular cross-section, the inner diameter should be half the outer.

Tubular solders are produced by pressing. Figure 41 illustrates the schematical view of a solder press. In pressing, the solder inserted into the mold 1 is forced by the punch 2 into the gap between the mouthpiece 4 and the shaped die 5; the so-formed tube-solder is filled by means of the mouthpiece 4 with molten flux kept in a separate container from which it is drawn into the tube. The size of the outer diameter of the tube is determined by the size of the shaping die 5, whereas the inner diameter depends on the position of the mouthpiece 4.

By means of this appliance, pressing can be done on a 50-60 ton press. Prior to pressing, the mold of the appliance is to be heated up to 130°C and the flux container, up to 140°C. The appliance is then charged with molten solder.

Solders of a eutectic or close-to-eutectic composition may be prepared not only as a finished alloy but also in the form of a mixture or of two-layer or multi-layer sheets in which a eutectic forms during heating. Such a solder is useful, e.g., where the eutectic alloy, owing to its low plasticity can hardly be prepared in a foil or wire shape. In such cases, it is feasible to

obtain a eutectic structure by heating its components or the intermediate alloying constituents up to a temperature, slightly above the melting point of the eutectic. The shape of such solders varies within large limits. Most commonly used are mixtures compounded of powder or paste; e.g., it is more easy to prepare solders representing a $\text{Cu}_3\text{-P}$ eutectic from a mixture of copper powder and phosphorous copper (Cu_3P), than by mechanical deformation of a finished low-plastic alloy.

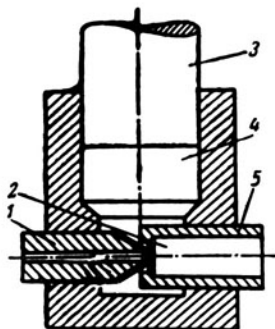


Figure 41. Schematic view of a molding press for the manufacture of tubular solders

Certain binary or more complex low-plastic eutectic solders may be used in the form of multilayer metallic or alloy strips, mutually bonded, for instance, by rolling. Eutectic Ag-Al solders can be used in the form of two silver and aluminum strips pressed together and then heated, which assures a diffusive bond without formation of a eutectic. The thickness of the composite strip should be chosen in such a manner that during the melting process, a eutectic or an alloy of given composition should be formed in all portions throughout the strip. Such a composite strip has much more plasticity than strips of a eutectic alloy.

Strip solders may consist not only of diffusion-bonded eutectic components, but also of two or more alloys. The process of manufacturing such strips of multicomponent A-B-C-D eutectic alloys may schematically be represented in the following way: if two alloys of the A-B and C-D or A-B-C and D system form, in a certain volumic proportion, an A+B+C+D eutectic, they are plastically deformable and the composite strip of these intermediate alloys will also be plastic after pressing or rolling and diffusion heating up to a temperature below the melting point of the eutectic. Pressing of the strip may be achieved particularly by its slow motion through the furnace at the temperature of diffusion heating. By such a procedure, 34A solders may be prepared in the form of two composite strips of silumin and copper, sintered at a temperature below the melting point of the ternary eutectic Al-Cu-Si (525°C)

Solders of a eutectic or a close-to-eutectic composition may be used also in the form of electrolytic or chemical coatings obtained in special baths (e.g., chemically deposited Ni-P alloys).

§ 1. Solders on a Bismuth Base

Bismuth is a low-plastic metal and therefore unsuitable for soldering of metals and alloys. Its melting point is 271°C . Bismuth forms with many metals low-melting eutectics which may be used as a soldering alloy, but owing to their scarcity they did not find wide use. Bismuth-rich alloys are used as solders with a solidus temperature ranging from 46.7 to 144°C .

The lowest temperature of the solidus in other non-bismuth low-melting alloys is 143°C (in case of the eutectic Pb-Sn-Cd). Table 9 lists compositions of bismuth-rich eutectics.

Only low-melting bismuth alloys and solders are of commercial use, particularly as fusibles in fire-extinguishing equipment and in electrical devices.

Bismuth-containing solders have a low-wetting action on some metals. Their wetting power may be improved by galvanizing these prior to soldering.

Table 10 presents some bismuth alloys, also proposed as solders.

Antimony added to bismuth alloys, increases their mechanical strength but reduces their plasticity.

Bismuth alloys have two peculiar features which are utilized in the manufacture of different parts. In the first place, when bismuth and bismuth-rich alloys pass from the fluid into the solid state, the volume of the solid phase is not reduced as in most of the other alloys, but on the contrary it shows a certain increase. Secondly, during aging of some bismuth alloys in the solid state, they are considerably expanded, the amount of this expansion exceeding the value of the thermal contraction. As a result, such alloys do not exhibit shrinkage phenomena; on the contrary their volume may increase upon solidification. This fact is sometimes used in various devices (e.g. for fastening punches to stamping dies). Figure 42 shows the change in length of a cast specimen of NSh-1-alloy in the process of its cooling (according to N. F. Lashko).

§ 2. Indium-base Soldering Alloys

The melting point of indium is 156.4°C . Combined with five other low-melting metals (Ia, Sn, Pb, Cd and Bi), indium forms very low-melting eutectics, starting bases for solders.

Indium has some peculiar features: certain indium-bearing alloys being deposited on glass wet it, forming with it a relatively strong bond; several indium alloys possess a high corrosion resistance in alkaline solutions.

The melting point of the eutectic solder composed of 52% In and 48% Sn is 117°C ; this solder wets glass and adheres to it /7/.

The low-melting ternary alloy with a 25% In content, 37.5% Pb and 37.5% Sn, is used particularly for the soldering of glass and quartz objects, on which a thin metallic film is deposited to assure a rigid bond; other types of solders may damage this film. Soldering is accomplished without flux /8/.

Many solders, among them solders on a tin-lead base, owing to their

reduced corrosion resistance are inadequate for soldering parts working in alkali media, (particularly in a KOH solution). On the other hand tin-lead and pure lead solders with a minimum In content of 25% /9/, have a high corrosion-resistance. Such solders have the following composition: 1) 37.5% Sn, 37.5% Pb, and 25% In; 2) 75% Pb, and 25% In. The wetting power of these solders is not smaller than of tin-lead solders (containing no indium). The crystallization interval of the first of these solders ranges from 135 to 180°C, the solidus of the second, being 230°C.

Table 9

Low-melting bismuth-rich eutectics

Composition of eutectic in %						Melting point in °C
Bi	Cd	Pb	Sn	In	Zn	
60	40	-	-	-	-	144
57	-	-	43	-	-	138.5
56	-	-	40	-	4	130
55.5	-	44.5	-	-	-	124
53.9	20.2	-	25.9	-	-	102.5
52	-	32	16	-	-	95
51.65	8.15	40.2	-	-	-	91.5
57.5	-	-	17.3	25.2	-	78.8
49.5	10.1	27.3	13.1	-	-	71
49.4	-	18.0	11.6	21.0	-	58
44.3	5.3	22.6	8.3	19.5	-	46.7

Table 10

Non-eutectic bismuth solders

Composition of solder in %				Temperature in °C	
Bi	Sn	Pb	Cd	Solidus	Liquidus
50	25	25	-	95	125
50	22	28	-	95	120
40	20	40	-	95	120
50	19	31	-	95	100
50	-	43	7	91.5	115
42	-	42	16	91.5	130

Despite their scarcity, indium-base solders will probably find a wider use in the soldering technique, particularly in soldering of vacuum equipment.

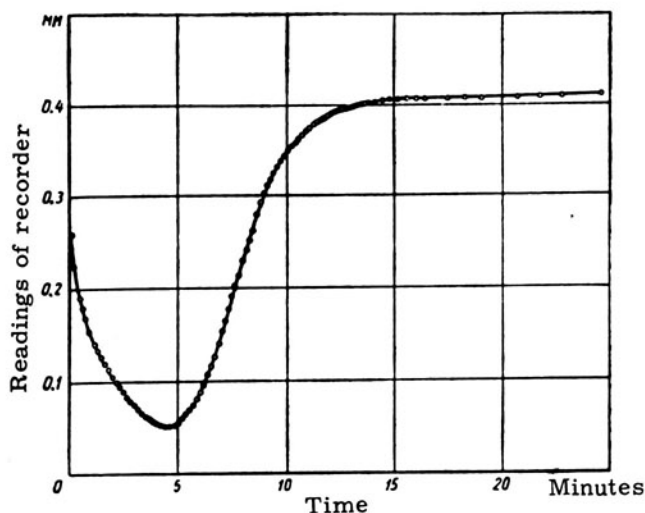


Figure 42. Change in length upon cooling, of a cast specimen of the NSh-1 alloy containing 48% Bi, 15% Zn, 32% Pb and 5% Sb

At present, vacuum glass seals are soldered with indium rich tin-solders, and particularly with eutectic solders (52% In and 48% Sn). These solders are employed without fluxes and applied by rubbing. As it was shown, bismuth, lead and cadmium-base solders with a rather high content of indium, are also suitable for the same purpose but their temperature range is more limited than that of tin-indium solders [8].

Certain eutectic indium alloys, listed in Table 11, present some interest as soldering alloys.

§ 3. Tin-Lead and Tin-Zinc Solders

Tin and tin-lead solders have the widest industrial use.

The most popular solders of this group have the following composition: 1) 50% Sn and 50% Pb; 2) 33% Sn and 67% Pb. This group of solders has gradually been completed with solders containing more or less tin.

Owing to the limited deposits of tin ore and its non-uniform occurrence in the earth's crust, zinc alloys with a small content of tin have been more investigated.

Tin-lead solders are standardized. The basic assortment of standard compositions is quite the same in different countries; generally these solders differ only in the amount of grades available and in the content of impurities.

Due to its hardening effect, antimony is added to tin-lead solders, but its content should not exceed 7%, since at a greater content, SnSb-intermetallic compounds are formed causing embrittlement of the solder. Antimony-bearing tin-lead solders are not suitable for the soldering of zinc and its alloys, since very brittle intermetallic compounds are formed. Addition

of antimony to solders allows the use of reclaimed tin and lead. Antimony reduces the oxidation of tin-lead solders in the liquid state and improves the external aspect and the heat resistance of these solders.

Table 11

Indium-bearing eutectic alloys with a melting range
from 90 to 141°C

Composition of the alloy %				Melting point °C
In	Cd	Sn	Zn	
44.2	13.6	41.4	0.8	90.0
44	14	42	-	93
52.2	-	46	1.8	108.0
74	24.25	-	1.75	116.0
52	-	48	-	117.0
27	73	-	-	123.0
98	-	-	2	141.5

Antimony lowers the fluidity, corrosion resistance and bonding ability of tin-lead solders, (particularly in soldering of galvanized coatings) and leads finally to embrittlement of the soldered joint. For special cases of soldering, the antimony content of tin-lead solders should not exceed 0.5%; for common soldering a content of up to 3% is permitted.

In order to save tin and to increase the mechanical strength of soldered parts not requiring a high degree of plasticity, GOST (All-Union State Standard) replaces tin-lead solders by solders of the POSS 4-6 type with a 6% Sb content. In certain cases, this type of solder exhibits no worse qualities than solders with a content of 40% Sn /10/.

Tables 12 and 13 show composition, use and properties of the Soviet-Standard tin-lead solders.

These solders are used for the following purpose:

POS90—for soldering of inner seams in food-vessels (electrical tea-kettles, various pans, etc.) and in medical equipment.

POS50—for soldering aviation radiators.

POS40—for soldering brass, iron and copper conductors.

POS30—for soldering brass, copper, iron, galvanized and zinc-plated sheets, tin-plates, aircraft radiators, various devices and radio-equipment, hoses and wire for armature bands of electro-motors.

POS18—for soldering lead, iron, brass, copper and galvanized-iron; for tinning iron prior to its soldering; for soldering of auto- and tractor-equipment and consumer's goods; it is also used as a substitute for the POS40 solder.

POSS4-6—for soldering of tinplates; iron, brass, copper and lead in case of lock-seams; for levelling (surfacing) welded seams and filling-in indentations in motor-car bodies, etc.; as a substitute for POS30 solders.

By adding lead to tin the strength of tin-lead solders gradually increases attaining the value of a eutectic composition but lowers with increasing addition of lead. According to some researchers, the maximum strength does not correspond to a eutectic alloy but to an alloy with ~73% Sn /12/. Apparently, the alloys used by these researchers were not chemically pure, thus

affecting the results. The plastic properties of the Sn-Pb alloys depend little on the composition (Figure 43).

Table 12

Composition of tin-lead solders*

Grade of solder	Composition of solders, %			Maximum amount of impurities		
	Tin Sn	Lead Pb	Antimony Sb	Copper Cu	Bismuth Bi	Arsenic As
POS90	89-90	remainder	≤ 0.15	0.08	0.1	0.05
POS61	59-61	idem	≤ 0.8	0.1	0.1	0.1
POS50	49-51	"	≤ 0.8	0.1	0.1	0.1
POS40	39-40	"	1.5-2.0	0.1	0.1	0.05
POS30	29-30	"	1.5-2.0	0.15	0.1	0.05
POS18	17-18	"	2.0-2.5	0.15	0.1	0.05
POSS4-6	3-4	"	5-6	0.15	0.1	0.05

* The maximum admissible amount of iron and sulfur is 0.02 %; of zinc and aluminum, 0.002 %; of nickel in POS90, POS61 and POS50 solders, 0.02 %; in the other solders, 0.08 %.

Table 13

Composition of tin-lead solders /11/

Grade of solder	Temperature of		Solidifying range °C	Specific gravity g/cm ³	Tensile strength kg/mm ²	Relative Elongation %	Impact strength kg/mm ²	Shear strength kg/mm ²	Proportionality limit under compr. kg/mm ²	Electric conductivity, % of pure copper	Fluidity (sand cast) cm	Brinell hardness kg/mm ²	Capillarity mm	Wettability mm
	Liquidus °C	Solidus °C												
01	232	232	0	7.31	1.9	43	5.29	2.19	1.7	13.9	125	6.2	31.7	225
POS90	222	183	39	7.57	4.3	25	1.85	2.70	3.5	-	135	13.0	-	-
POS50	209	183	26	8.83	3.6	32	4.59	3.54	2.9	11.0	115	15.6	23.8	966
POS40	235	183	52	9.31	3.2	63	4.75	3.67	2.8	10.2	91	12.6	23.8	1130
POS30	256	183	73	9.69	3.3	5.8	4.67	2.90	2.8	9.5	63	10.1	25.4	1038
POS25	265	183	82	9.94	2.8	52.1	3.68	2.85	2.6	9.1	-	10.5	-	-
POS18	277	183	94	10.23	2.8	67.0	3.86	2.52	2.3	8.6	60	10.5	14.0	640
POSS4-6	265	245	20	10.7	5.9	23.7	0.8	-	-	-	-	14.2	-	-
S1	327	327	0	11.37	1.1	4.5	2.11	1.27	0.2	7.9	1.34	2.3	14.2	167

Tin has two polymorphic forms: 1) white β —tin with a tetragonal crystalline lattice, heat-resistant at a temperature range from 13.2 to 232°C; its specific gravity is 7.28 g/cm³; 2) gray α —tin with a cubic crystalline lattice, resistant to temperatures below 13.2°C and having a specific X-ray measured gravity of 5.8 g/cm³.

Transformation of white in gray tin is accompanied by liberation of heat and by large changes in volume, which leads to a certain discontinuity (formation of gray powder) in the volume of tin.

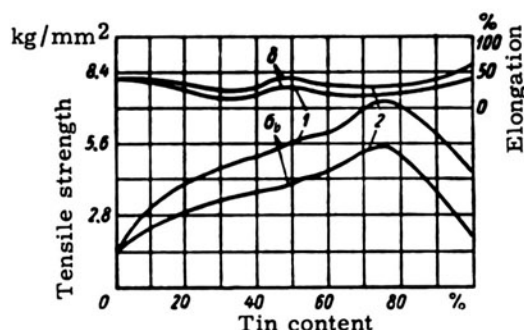


Figure 43. Tensile strength σ_v and elongation δ of Pb-Sn solders to which antimony is added (1) or not added (2); (the ratio of added antimony, Sb/Sn = 0.2)

In contrast to the polymorphic transformation of many other metals, the polymorphic $\beta \rightarrow \alpha$ transformation of tin may be impeded.

Thanks to the tendency of tin to be suprasaturated, the rate of transformation of white in gray tin at 13.2°C is low; it attains a maximum value at a range from -30°C to -50°C [13/-15] and lowers with the further reduction of temperature.

The transformation of white in gray tin is speeded up in the presence of: gray tin-nuclei, stresses, a corrosion-active medium, some impurities; the pressure exerted by the surrounding medium also speeds up the transformation. The transformation is also fostered by repeated heating and cooling [16/.

Aluminum and zinc promote decomposition of white tin; bismuth, antimony and lead have a retarding action. At a content of 0.3–0.5% Bi or ~0.5% Sb or 1% Pb, decomposition of tin becomes practically impossible.

The polymorphic $\beta \rightarrow \alpha$ transformation of tin proceeds much slower during tinning as compared with electroplating [17/]. Since the electroplated layer of definite thickness has a greater amount of grains than the chemically tinned layer, the decomposition of white tin (the so-called tin pest) is accelerated.

In tin-lead solders and in their soldered seams, tin "pest" could not be noticed even when exposing the soldered joints to low temperatures.

In lead-tin solders tin occurs in the form of an independent excess phase or of a phase included in the Sn-Pb eutectic. The behavior of white tin at low temperatures essentially differs from that of lead.

White tin shows a certain cold-brittleness when subjected to impact testing at low temperatures; at a temperature from -30° to -60°C, the tough fracture changes into a brittle one [18/ (Figure 44). Lead exhibits no cold-brittleness when exposed to impact tests, regardless of the temperature at which it was tested.

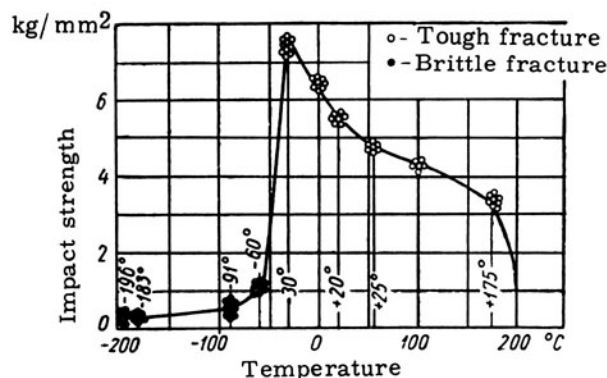


Figure 44. Variation of tenacity of tin with the temperature

The temperature range of the transition from the tough to the brittle state of a POS40 solder subjected to impact testing is almost the same as in pure tin solders. When a POS30 solder with an amount of the phase smaller than that of the POS40 solder is subjected to impact tests the temperature range of the transition from the tough to the brittle state will be enlarged, whereas the reduction of the impact strength will show a smoother course. When the basic phase of lead-tin solders is formed by a lead-base solid solution, while the tin phase appears in the form of inclusions, the brittle range will not be noticed (at a tin content of ~15-20%).

The tensile strength and plastic properties (elongation and compressive strength) of lead and its alloys increase with the reduction of temperature, whereas the change in the mechanical characteristics of tin and its alloys has a more intricate character. Reduction of the temperature of tin from 140 to 17°C is at first associated with a certain rise in its strength, but, with further lowering of the temperature, the strength is reduced. Starting from about -120°C, the plasticity of tin undergoes a sudden reduction. In tin-lead alloys (up to ~50% Pb), maximum strength can be noticed at various temperatures (Figure 45) /19/.

When the temperature of lead-tin solders is reduced below the room temperature, their plasticity (Figure 46) is gradually reduced; in these solders, lead occurs in the form of an isolated phase. Only in Pb-Sn solders (with a content of 15-20% Sn), in which tin forms an isolated phase, the reduction of temperature increases strength and plasticity /20/.

Table 14 presents some data about the testing of tin-lead solders at various temperatures.

As shown by the data (mentioned in Table 14) on the properties of lead-tin solders at low temperatures, the use of tin-rich solders may cause embrittlement of soldered joints exposed to low temperatures.

Tin-lead and tin-cadmium solders possess two important characteristic features which determine the final mechanical properties of the soldered joint: 1) The temperature of crystallization is close to the room temperature; 2) The solubility of tin in lead greatly varies with the increase in

temperature. At the room temperature, lead dissolves 2% Sn, while at the eutectic temperature of 183°C , 19.5% Sn are dissolved in the Pb-Sn system.

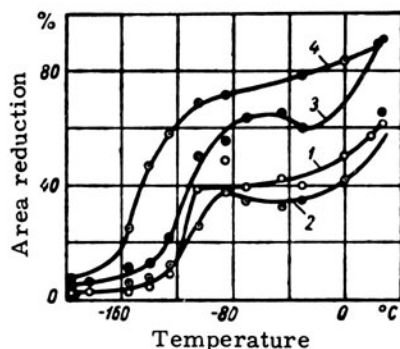


Figure 45. Variation of area reduction in tensile-tested alloy specimens with the temperature:

1—5% Pb; 2—10% Pb; 3—38.7% Pb; 4—50% Pb.

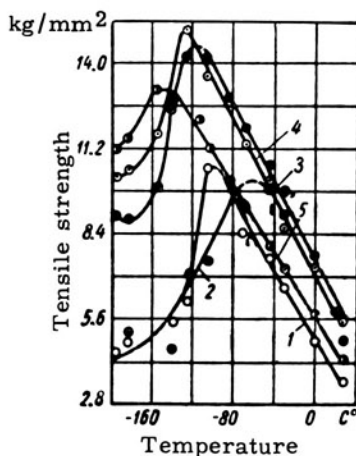


Figure 46. Variation of tensile strength of Sn-Pb alloy specimens with the temperature:

1—1% Pb; 2—1.66% Pb; 3—5% Pb; 4—10% Pb; 5—38.7% Pb.

These solders cannot be hardened by cold-working. In contrast to pure tin, cold worked lead-solders have a smaller hardness and strength than in the cast form. As detailed investigations have shown, this phenomenon is caused not only by the low temperature of the crystallization process but also by the separation of tin from the supersaturated solid solution of lead. Deformation of solders favors (speeds up) decomposition of solid

solutions and coalescence of the structural components; this is accompanied by a considerable softening of the alloys involved. Softening induced by decomposition of the supersaturated solid solution (mainly in solutions of tin in lead), prevails over the hardening effect caused by the disturbance of the cast structure; the strength of such solders in contrast to many other solders is lower in the deformed state than in the cast form. This fact could be revealed in a eutectic solder containing 72% Ag and 28% Cu, after its deformation at elevated temperatures; in these types of solders, solubility of silver and copper noticeably changes with the increase of the temperature.

Table 14

Mechanical properties of tin-lead solders
at low temperatures /21, 22/

Composition of solder in %		Tensile strength in kg/mm ² at a temperature of °C			Area reduction in % at a temperature of °C		
Sn	Pb	+17°	-196°	-253°	+17°	-196°	-253°
100	-	3.6	7.1	7.3	91	4	0
90	10	5.4	11.0	14.0	-	18	2
60	40	5.6	12.0	15.0	49	6	1
50	50	5.6	13.0	16.0	66	63	6
25	75	5.2	13.0	17.0	87	27	21
-	100	2.8	4.5	7.1	100	100	100

After casting, tin-lead solders continue to be in a non-equilibrium state. Heating of these solders induces in them an aging process. The high rate of diffusion of the alloying constituents at room temperature and slightly above it, leads to the fact that, when investigating the mechanical properties of these solders after their aging, a super-aging phase (which is practically negligible) is always noticeable. A more visible super-aging effect (softening) is observed when lead-tin solders are heated over the range from 100 to 150°C /23/.

A great variety of substituents for tin-lead solders has been suggested. Table 15 presents certain substitute-solders in which tin has been replaced by cadmium. These solders are of the ternary type and form, upon crystallization, a ternary Pb-Cd-Sn eutectic with the melting point at 145°C.

Several tin solders are alloyed with a certain amount of zinc (Table 16). Solders with a zinc content of 10–30%, are chiefly used in tinning of aluminum and its alloys by means of ultrasonic soldering torches or in an ultrasonic bath. Solders with 10% Zn are rather eutectics (the Sn-Zn eutectic contains 9% Zn).

Addition of ~1% Ni increases the heat resistance of eutectic solders; silver added in a quantity up to 1.5–2% improves the technological properties of these solders.

Inclusion of silver in tin-lead solders favors the building up of a fine-grained structure.

Table 15

Cadmium-bearing solders as substitute for tin-lead solders
/11/, /24/, /27/

Composition of solder %			Temperature of		Composition of solder %			Temperature of	
Pb	Cd	Sn	Solidus °C	Liquidus °C	Pb	Cd	Sn	Solidus °C	Liquidus °C
68	9	23	145	235	75	22	3	145	237
75	10	15	145	245	65	26	9	145	225
80	10	10	145	253	27.5	6.5	66	145	172
85	5	10	145	260	13.5	21.5	65	145	160
88	2	10	145	275	25	25	50	145	160
85	10	5	145	257	32	18	50	145	145

Table 16

Tin-lead solders

Composition of solder %				Temperature °C		Remarks
Sn	Zn	Ni	Ag	Solidus	Liquidus	
90	10	-	-	199	205	P-200
90	20	-	-	199	280	P-250
90-92	8-9	0.75-1.25	-	219	232	-
68-69.5	29-30	-	1.5-2	260	280	4223-1 /28/

§ 4. Tinless Lead-Base Solders

Pure lead is inadequate for soldering purposes since with most metals it does not form stable compounds. With copper, iron, cobalt, nickel, aluminum, zinc and magnesium, lead forms instable compounds.

Binary or more complex alloyed lead-bearing systems, forming simple eutectics, may be used as solders.

Besides the Pb-Sn eutectic, the following eutectics are of real importance for solders with a minimum melting point of 125°C: 1) 43.5% Pb and 56.5% Bi (melting at 125°C); 2) 82.5% Pb and 17.5% Cd (melting at 248°C); 3) 97.5% Pb and 2.5% Ag (304°C); 4) 87% Pb and 13% Sb (247°C); 5) 99.5% Pb and 0.5% Zn (318.2°C); 6) 28.6% Pb and 16.7% Cd, 52.45% Sn and 2.25% Zn (138°C); 7) 32% Pb, 18.2% Cd and 49.8% Sn (145°C); 8) 24% Pb, 71% Sn and 5% Zn (177°C); 9) 81.7% Pb, 17.3% Cd and 1% Zn (245°C).

Table 17

Characteristics of lead solders /27/, /29/.

Composition of solder, %					Temperature in °C of		Strength, 2 in kg/mm ²		Losses in % ZnCl ₂ for 20 sec	Tinning of copper
Pb	Cd	Zn	Ag	Sb	Solidus	Liquidus	Soldering	Shear	Tensile	
91.5	8.5	—	—	—	248	276	336	9.2	4.9	Satisfactory
90	10	—	—	—	248	274	334	9.7	5.0	The same
80	20	—	—	—	248	259	319	9.4	5.7	" "
70	30	—	—	—	248	260	320	9.8	4.5	" "
90.8	7.8	1.4	—	—	237	267	327	11.5	5.2	" "
87.5	7.5	5.0	—	—	235	368	428	7.6	4.1	" "
79.7	17.7	—	—	2.6	—	239	299	10.2	5.0	" "
97.5—98*	—	—	2.0—2.5	—	304	308	364	6.6	3.1	Good
94—95*	—	—	5.0—6.0	—	304	365—380	425	6.4	2.9	Satisfactory

* An aqueous solution containing 40 % ZnCl₂ and 20 % NH₄Cl, the remainder—water, may be used for fluxing purposes.

The Pb-Sb eutectic is rather brittle and exhibits a poor coherence with copper; lead solders contain only a small amount of antimony which increases their hardness. The basic components of lead solders, besides tin, are cadmium, silver, partially zinc or antimony. Table 17 covers some lead-base tinless soldering alloys.

Other types of lead-base solders with a certain content of tin and cadmium are also in use. Among them the following solders may be mentioned: 1) 99.5% Pb and 0.5% Zn; 2) 99% Pb, 0.5% Zn and 0.5% Mn; 3) 99% Pb and 1% Zn; 4) 98% Pb, 1% Zn and 1% Cd; 5) 98% Pb and 2% Zn; 6) 96% Pb, 2% Zn and 2% Cd /11/, /30/ and /31/.

Table 18

Tensile strength of copper, brass or steel joints soldered with SK-7 solders and with standard POS30 and POS40 solders (at different temperatures)

Grade of solder	Tensile strength of soldered joints (in kg/mm ²) of various materials								
	Copper			Brass			Steel		
	20°	-70°	+100°	20°	-70°	+100°	20°	-70°	+100°
POS30	3.8-5.1	5.9-7	1-2.3	3.3-3.9	3.8-4.6	1.6-2.3	3.2-4.5	6-7.6	1.2-2
POS40	3.8-6	6.5-7.2	0.9-2	3.6-4.3	4.2-5.0	1.2-1.9	3.1-5.1	6.8-8.2	1.3-2.4
SK-7	2.8-3.8	5.7-6.2	2.1-3.5	3.1-4.0	4-5	1.6-3.2	2.9-3.5	4.5-5.5	0.9-2.4

For the production of solders the ability of certain elements to cause hardening of lead has been resorted to. Such elements are cadmium, zinc, silver, antimony and also sodium /32/. Of the alloys belonging to the Pb-Cd-Zn-Sb-Na system investigated by the authors of the present study, of definite importance are the SK-7 solders of the following composition: 6-10% Cd, 0.5-1.5% Zn, 1.0-1.5% Sb, up to 0.3% Na and the remainder, lead; the melting point of this alloy is 270°C.

The tensile strength of the cast SK-7 solder is 10-13 kg/mm² (i.e. twice the strength of the POS30 and POS40 solders); the elongation amounts to 0.4% (i.e. one twentieth of that of the POS30 and POS40 solders), (Table 18). The tensile strength of butt-soldered joints is given in Table 19.

For soldering, fluxes were used of the following composition: 11% NaCl, 14% KCl, 65% ZnCl₂ and 10% NH₄Cl.

A lead-base close-to-eutectic alloy containing 12% Sb and 0.5% As /33/ has been suggested as a substitute for tin-solders. It has a narrow crystallization range (245-246°C), a tensile strength of 4.3 kg/mm², an elongation $\delta = 101\%$ and an area reduction of $\psi = 94\%$. This alloy assures good soldered joints on iron and steel and poor joints on copper and brass. The shear strength of iron joints soldered with this solder is 5.8 kg/mm². Arsenic is added in order to reduce the oxidability of the solder and to create a fine-grained structure.

§ 5. Cadmium-Base Solders

Cadmium possesses a relatively high corrosion resistance. In the pure form it hardly will find a wider use as a soldering metal.

Table 19

Tensile strength of copper, brass and steel-specimen butt joints
soldered with POS30, POS40 and SK-7 solders

Soldered metal	Tensile strength when various solders have been used, kg/mm ²		
	POS30	POS40	SK-7
Copper	4.0-8.1	8.7-13.7	4.0-6.0
Brass	6.4-12.7	6.5-11.6	3.7-5.4
Steel	7.1-12.5	2.0-10.2	2.0-6.7

Cadmium has been used for soldering preliminary brass-plated steel rims of electrical machines. For fluxing, a colophony-alcohol mixture has been employed.

During crystallization of iron or aluminum-bearing cadmium alloys, two laminated layers are set up. In the solid state, cadmium has a reduced interaction with steel and aluminum.

As the study of binary equilibrium-diagrams has shown only a limited number of cadmium binary-alloys may be used as a base for solders. Among them five binary systems with a simple eutectic structure should be mentioned: 1) Cd-Bi (melting at 144°C with 40% Cd); 2) Cd-Zn (melting point of eutectic 266°C for a content of 82.6% Cd); 3) Cd-Pb (melting point of eutectic 248°C for a content of 17.5% Cd); 4) Cd-Sn (melting point of eutectic 177°C for a content of 32.25% Cd); 5) Cd-Tl (melting point of eutectic 203.5°C for a content of 17% Tl). Such eutectics usually have a higher plasticity than eutectics with chemical compounds (see Table 20). In the Cd-Sb system a brittle eutectic is formed (melting point of eutectic 285°C at a content of 92.5% Cd).

Several types of cadmium solders with small quantities of impurities are known.

Cadmium-silver solders have a great creep resistance, and are easily deformable. Their tensile strength is higher than that of Sn-Ag and Pb-Ag alloys; the tensile strength of a cadmium solder with 5% Ag varies within the limits of 11.3-13.3 kg/mm²; that of the cadmium solder with 16% Zn and 5% Ag is 20.5 kg/mm² /34/.

In a series of solders, tin is partially or totally replaced by cadmium. As a rule, these are binary (Pb-Cd) or ternary (Pb-Cd-Sn) alloys.

Measures should be taken to avoid evolution of extremely poisonous brown vapors of cadmium oxides during manufacturing cadmium-rich solders; during soldering, the solder should not be overheated. Melting of such solders in an inclined position is not allowed.

The soldering temperature of cadmium bismuthless solders exceeds the range of bismuth solders and covers the interval from 145°C to 440°C. In this temperature range, four sub-ranges are distinguished: 1) 145-275°C for ternary Pb-Cd-Sn solders; 2) 248-275°C for binary Pb-Cd solders; 3) 266-335°C for Cd-Zn solders; 4) 300-440°C for Cd-Ag; Cd-Ag-Zn-Ni; or Cd-Ag-Sn solders.

Table 20

Characteristics of some cadmium solders

Composition of solders %					Temperature °C of	
Cd	Zn	Mg	Sn	Ag	Solidus	Liquidus
82.6	17.4	-	-	-	266	266
50	50	-	-	-	266	326
79	16	-	-	5	270	285
96.7-94.8	0.8-1.7	-	-	2.5-3.5	320	340
97.47-96.42	-	0.03-0.08	-	2.5-3.5	320	349
50	20	-	30	-	157	277
65	30	-	5	-	229	294
60	30	-	10	-	-	332

§ 6. Low-Melting Heat-Resistant Solders

When Zn—Pb solders and the resulting joints are subjected to the action of applied stresses, they are liable to change their sizes (due to creep) even at room temperatures /35/, /36/. The creep of these solders and of the resulting joints depends on the degree of crystallization, on the composition and on the base metal involved. Course-grained solders (like other alloys) have a greater creep-resistance than fine-grained solders /36/. A tin solder with 3% P has a greater creep-resistance at 20 and 80°C than Sn—Pb solders /2/. Addition of antimony to tin-lead solders increases their mechanical strength and creep-resistance; addition of small quantities of copper has the same effect.

Lapped joints soldered with tin-lead solders have a different degree of creep resistance in the following sequence of the soldered base metals: steel, copper, brass. Of particular importance here is the alloying process in the solder during soldering, owing to the dissolution of the base metal in the molten solder (see Table 21).

Cadmium additions to tin increase the endurance limit at a temperature up to 20°C. At a temperature higher than 20°C, the endurance limit of the Sn—Sb eutectic is higher than of the Zn—Pb eutectic.

Considerable hardening of the solders can be achieved by adding up to 5% Ag (see Table 22) /37/, /38/.

Addition of antimony to tin solders at temperatures above 100°C imparts to them heat resistance.

Heat resistant lead-bearing solders contain 2.5% Ag and correspond to the eutectic Pb—Ag alloy with a melting point at 298°C (PSr3).

These types of solders have the following mechanical properties: Brinell hardness, 9.2 kg/mm²; impact strength, 2.66 kg/mm²; tensile strength 3.1 kg/mm²; elongation 45%. The tensile strength at 200°C is 1.15 kg/mm², and at 250°C 0.59 kg/mm². The tensile strength of a butt-soldered copper joint is 5 kg/mm².

Table 21

Creep resistance at room temperature of various joints
soldered with tin-lead solders /36/

Composition of solder, %				Properties of soldered joint		
Sn	Sb	Cu	Pb	Applied stresses causing an elongation of $1.10^{-4}\%$ 24 hours after the test, kg/mm^2	Base metal or alloy	Endurance limit (after 500 hours) kg/mm^2
44	-	0.009	55.991	0.1	Steel Copper Brass	0.15 0.22 0.53
44	-	0.09	55.91	0.28	Steel Copper Brass	0.22 0.22 0.53
40	2	0.09	57.91	0.30	Steel Copper Brass	0.23 0.27 0.53

Another solder of this system, containing 6% Ag, has a higher shear resistance at 195°C than solders with 50% Sn and 50% Pb (Table 23) /39/.

Among the low-melting tin, lead and cadmium-base solders, silver-bearing cadmium solders have the highest strength and heat resistance. Table 24 presents data on the strength of Cd-5% Ag solders at various temperatures /40/.

For soldering the wire-ends of armature-winding coils, joined to the commutator-lugs and to the compensating connections of electrical machines, A.I. Shpagin and A.B. Slonimskii proposed a 3% Ag cadmium solder. In order to reduce oxidation of the alloy in the molten condition by an amount of 0.03-0.08%, magnesium (the K-3 solder) or 0.8-1.7% Zn (the K-1 solder) is to be added to the solder.

Table 25 presents some properties of cadmium solders in comparison with tin solders and heat-resistant PSr-3 solders (according to A.I. Shpagin and A.B. Slonimskii).

The shear strength of copper butt-joints soldered with a K-3 solder is 5.2 kg/mm^2 , and with a K-1 solder, 7.5 kg/mm^2 ; the shear strength of copper alloys soldered with a K-3 solder is 4.8 kg/mm^2 and with a K-1 solder, 5.9 kg/mm^2 .

Table 26 presents low-melting silver solders having multicomponent bases.

These solders allow the presence of impurities (Cu, Bi, Sb or As) up to 0.5% and find application in soldering of radiators and other parts working at elevated temperatures.

Table 22

Variation of tensile strength and plasticity of tin solders
at different temperatures (up to 200°C)

Testing temperature in °C	Tensile strength and elongation σ_v of various tin-base solders						Elongation of 96 % Sn and 4 % Ag σ_v in kg/mm ²
	60 % Sn and 40 % Pb		40 % Sn and 60 % Pb		95 % Sn and 5 % Sb		
	σ_v in kg/mm ²	δ in %	σ_v in kg/mm ²	δ in %	σ_v in kg/mm ²	δ in %	
20	5.75	60	5.35	55	4.17	43	5.51
50	4.73	80	4.41	72	3.94	45	4.73
75	4.25	90	3.94	80	—	—	—
100	3.15	110	2.52	98	2.84	50	2.52
125	1.97	180	1.58	200	2.28	—	—
150	1.26	180	1.18	200	2.28	45	1.89
200	Melting		Melting		1.18	45	1.18
220	"		"		0.79	40	—

Table 23

Shear resistance of solders at various testing temperatures

Composition of solder	Shear resistance kg/mm ² at	
	20°C	195°C
94 % Pb and 6 % Ag	1.70	1.07
50 % Pb and 50 % Sn	1.78	0.44

Cadmium whose melting point is 321°C may be used as a base for heat-resistant solders. The latter are very important for the soldering of parts working at temperatures up to 350°C (e.g. radiators and parts of electrical machines).

Copper and brass joints soldered with cadmium solders that contain more than 5% Ag have a low plasticity and a small strength (1.5–2.5 kg/mm²). Improvement of the coherence of such solders with the parts to be soldered, may be attained by adding to the solder 2–7% Zn and 1–2% Ni. Solders of

this type are the following: PSr12K, PSr8KTsN, and PSr5KTsN (devised by the authors and their co-workers B.O. Katsman and K.I. Soshnikova).

Table 24

Mechanical properties of 5% Ag cadmium-solders
at various temperatures

Testing temperature °C	Tensile strength σ_v kg/mm ²	Elongation δ %	Area reduction ψ %
20	11.3	31.3	81.0
150	2.76	93.7	91.0
220	1.80	93.7	68.0
260	1.17	21.9	11.0

Table 25

Mechanical properties of cadmium solders

Grade of solder	Composition of solders, %					Tensile strength σ_v kg/mm ²			Relative elongation δ % at 20°C
	Cd	Pb	Zn	Mg	Ag	20°	200°	250°	
K83-17	82.6	-	17.4	-	-	12.3	-	-	25.8
K-1	90.7-94.8	-	0.8-1.7	-	2.5-3.5	13.5	3.5	0.8	-
K-3	97.45-96.45	-	-	0.05	2.5-3.5	11.5	4.1	3.2	40.0
PSr 3	-	97.5	-	-	2.5	3.1	1.2	0.6	45.0
Tin	-	-	-	-	-	2.6	0.3	0.0	46.0

Some data on these solders and the shear resistance of copper and brass joints soldered with them is given in Table 27 in comparison with the data on the 155-solder with 5-6% Ag, 1-2% Sn and the remainder Cd.

Despite the fact that some solders of the Cd-Ag-Zn-Ni system have only a small strength at temperatures higher than 250°C, the copper and brass joints soldered with these solders possess a sufficient shear resistance in the range from 250 to 350°C. This is connected with the diffusion of copper into the solder and with the formation in the seam of Cd-Ag-Cu-Zn-Ni alloys having a higher solidus and liquidus than the starting solders. Therefore, the PSr12K and PSr8KTsN solders may be adequate for soldering copper and brass-parts at temperatures from 250 to 350°C.

Soldering of copper and copper-alloy parts with the solders listed in Table 27, may be performed with LK-2 or LK-10 fluxes if the soldering temperature does not exceed 350°C. In rapid heating, e.g. by the electro-

resistance method, the LK-2 flux may be used in cases where the soldering temperature reaches 420°C. At a soldering temperature higher than 420°C, fluxes of the FK-30 type having the following composition may be used: 50% NaCl, 30% CdCl, 15% ZnCl₂ and 5% NH₄Cl.

Table 26

Low-melting heat-resisting solders

Grade of solder	Composition of solders in %				Crystallization range, °C	Specific gravity, g/cm ³
	Pb	Sn	Cd	Ag		
PSr2.5	9.2 ± 1.0	5.5 ± 0.5	—	2.5 ± 0.3	295-305	11.0
PSr1.5	83.5 ± 1.5	15 ± 1.0	—	1.5 ± 0.8	265-370	10.4
PSr2	63 ± 1.5	30 ± 0.1	5 ± 0.5	2 ± 0.3	225-235	9.6
	93.5	5	—	1.5	296-301	—
	97.5	1	—	1.5	309-310	—
	93-95	1-2	—	5-6	304-302	—

Table 27

Melting points and tensile strength of cast solders and of copper and brass joints soldered with cast solders, at elevated temperatures (for soldering of test-specimens, an LK-2 or K-30 flux has been used, heating being performed by the electro-resistance method)

Grade of solder	Temperature °C		Tensile strength (kg/mm ²) of solders, at °C			Electric conductivity in % of copper	Shear resistance (at various temperatures) of soldered joints kg/mm ²											
							20°		100°		200°		250°		300°		350°	
	Solidus	Liquidus	20	200	300		Copper	Brass	Copper	Brass	Copper	Brass	Copper	Brass	Copper	Brass	Copper	Brass
PSr12K	337	420	18	5	0	12.7	3.9	4.2	2.7	3.4	2.4	3.1	2.4	3.0	2.4	2.6	1.4	1.5
PSr8KTsN	330	410	17	5	0	21.2	4.9	4.4	3.4	4.5	3.2	3.1	1.1	2.1	0.6	0.9	-	-
PSr5KTsN	320	360	15	-	-	-	4.7	5.4	4.6	5.1	3.0	4.5	2.5	2.8	1.4	1.9	-	-
155	300	360	-	-	-	-	1.75	1.75	-	-	-	-	-	-	-	-	-	-

The eutectic Cd—Zn solder is required for soldering of Al—Mn bronze and of alloy steels. Its spreadability is rather reduced.

§ 7. Zinc-Base Solders

Of the four low-melting metals, tin, lead, cadmium and zinc, the latter occupies a particular position. Zinc has a relatively high melting point (419°C). Besides cadmium, apparently only on a zinc base, one may obtain solders with a solidus temperature of $350\text{--}500^{\circ}\text{C}$. Soldering in this range so far has been little investigated. At present, the use of solders in this temperature range is particularly important because such solders are required for soldering various radiators and commutators of electrical machines subjected to intense heating while in operation.

As investigation of the corrosion of Zn—Cd—Pb—Sn alloys has shown, the increase of the tin content leads to an increase of the corrosion resistance of these alloys.

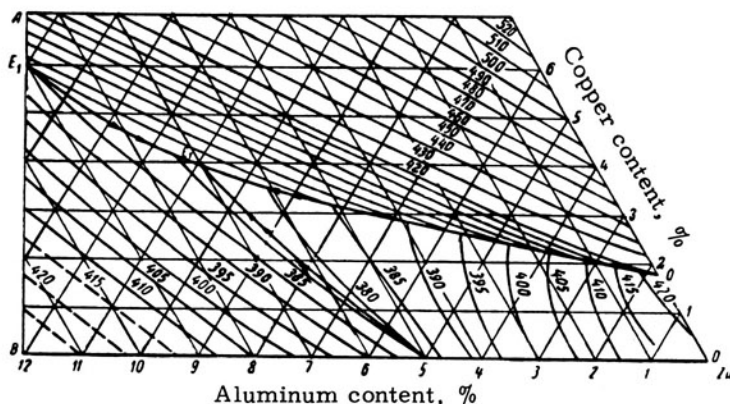


Figure 47. Surface of the liquidus region of the Zn—Al—Cu system with E, E₁, E_T—eutectics

Zinc forms with numerous elements eutectic systems, whose melting point determines the minimum temperature range of the tin-bearing solders.

Table 28 presents composition and melting point of a series of zinc-bearing solders.

Due to the relatively high fusibility of zinc as compared with cadmium, lead and tin, the eutectic alloys of the Zn—Cd—Pb—Sn system have only a small zinc content; therefore, zinc-base solders containing one, two or three of these elements have the highest melting point in the solid state (318.2°C). A higher soldering temperature may be obtained with solders of the Zn—Al or Zn—Al—Cu system (Figure 47). The melting point of the binary Zn—5% Al is 380°C and of the ternary Zn—Al—Cu system, 377°C .

By adding other alloying constituents, the solidus temperature of solders can be either lowered to 350°C or raised to 500°C .

Table 28

Composition and melting point of certain zinc-containing eutectics

Composition of eutectic, %							Melting point °C
Zn	Cd	Pb	Sn	Al	Cu	Sb	
2.25	16.7	28.6	52.45	-	-	-	138
2.5	31	-	66.5	-	-	-	163
5	-	24	71	-	-	-	177
8.9	-	-	91.1	-	-	-	198.6
1	17.3	81.7	-	-	-	-	245
17.4	82.6	-	-	-	-	-	266
0.5	-	99.5	-	-	-	-	318.2
89	-	-	-	7	4	-	377
95	-	-	-	5	-	-	380
94	-	-	-	-	-	6	411

Table 29 shows a series of solders with a Zn-content higher than 40 %. Certain solders are described in various studies, other zinc-base solders have been checked or devised by the authors of the present study.

According to the authors, the eutectic Zn-Al and Zn-Al-Cu solders have an insufficient spreadability and a reduced ability to fill in the gap between the parts to be soldered. Small additions of tin and lead (V-63 solders) assure a better filling of the gap (particularly in soldering of copper, aluminum and its alloys). Due to the great reactivity of zinc and its alloys with aluminum alloys and copper, the soldering clearance should be pretty large (0.20-0.25 mm).

The PTsAM-65 solder (devised by A.G. Shuvalov) and the 4223-2 solder (devised by V. M. Kozovkov) have satisfactory corrosion properties in soldered aluminum joints. The 4223-2 solder is suitable for soldering joints subjected to temperatures from -60° to +200°C (particularly for soldering aluminum conductors).

The 5, 10-13 and 18-solders are used in the abrasive-soldering process. They may be used in soldering aluminum and its alloys with P320A and 34A fluxes. Solders with a liquidus point below 400°C may be used in ultrasonic fluxless soldering or in abrasive soldering operations.

Due to their poor spreadability, zinc-base solders are unsuitable for soldering of copper, copper alloys and low-carbon steels. At present, for this purpose, solders of grade No. 7 or V-63 may be used together with the FTs37 flux of the following composition: 5% NaF, 37% ZnCl₂, 16% ZrCl₄, 31% KCl, 6% NaCl and 5% NH₄Cl to 30 cc H₂O.

The shear strength of copper and brass test-specimens lap-soldered with a V-63 solder and a Fts35 flux is ~ 4 kg/mm² and that of specimens soldered with P-480, and PtsAm-65 solders, 1.5-2 kg/mm².

§ 8. Magnesium-Base Solders

Magnesium-base solders are suitable for soldering magnesium alloys only, since as a rule, their use in soldering alloys of other bases, produces brittle, corrosion-unstable seams. An appreciable reduction of the melting point of magnesium may be achieved by addition of aluminum, zinc or cadmium; since many magnesium alloys contain zinc and aluminum, magnesium base solders also have a large amount of these elements.

For the time being, soldering of magnesium alloys is still of little use. Some magnesium-base solders are listed in Table 30.

The P430MG and P380MG solders have been devised by B.A. Maksimikhin and M.A. Nesterova.

Table 30

Magnesium-base Solders

Composition of solder, %						Tensile strength, kg/mm ²	Temperature, °C		Source of information
Mg	Al	Zn	Cd	Bi	Mn		Solidus	Liquidus	
83	12	5	—	—	—	—	—	500	[46]
88.998	9	2	—	0.002	—	—	—	595	[46]
73.9—	25—	1.0—	—	—	0.1—	9—12	—	435	[47]
71.2	27	1.5	—	—	0.3	—	—	—	—
53.8—	21—	0.2—	25—	—	0.1—	7—9	—	415	[47]
51.5	22	0.5	26	—	0.3	—	—	—	—
75—72.5	2.0—	23—	—	—	—	10—12	430	~ 600	P430MG
—	2.5	25	—	—	—	—	—	—	—
86.25—	0.75—	13—	—	—	—	13—15	380	~ 550	P380MG
84	1.00	15	—	—	—	—	—	—	—

§ 9. Aluminum-Base Solders

For soldering of aluminum-base alloys, only aluminum solders and its alloys are used at present, despite their relatively low fusibility as compared, e.g., with steels and copper alloys. The reasons for this restricted use are: difficulties in the removal of aluminum oxides during soldering and the unfavorable influence of a high aluminum-content on the properties of alloys prepared on another base.

Aluminum forms eutectics with many elements, but only a limited number of them may be used as solders. In many binary aluminum-alloys, the melting point of their eutectics differs little from the melting point of aluminum (660°C) and its alloys. Such alloys are the following: Al—Au; Al—Ba; Al—Be; Al—Ce; Al—Ca; Al—Co; Al—Fe; Al—La; Al—Ni; Al—Te; etc. The Al—7.5% Li eutectic has the melting point at 535°C and is expensive.

The four binary eutectics Al-Cu, Al-Mg, Al-Sn, and Al-Ag meet the requirements as to the melting point but not with regard to other properties.

The Al-33% Cu eutectic (melting point 548°C), and the Al-34.5% Mg eutectic (melting point 451°C) are brittle and corrosion unstable. The melting point of the Al-Sn eutectic is very low (229°C) but aluminum-rich tin-alloys are corrosion unstable, even in distilled water; due to the large range of crystallization during soldering aluminum and its alloys with Sn-Al solders, the soldered seam is liable to form hot cracks.

The Al-Ag solders have a relatively high corrosion-resistance, but they are expensive. Moreover, a sufficient reduction of the melting point of aluminum requires addition of much silver (the melting point of the eutectic with 72% Ag is 558°C). Reportedly, aluminum solders with 40% silver and a crystallization range from 430 to 535°C have been used for the soldering of aluminum alloys [48]. Most suitable to form bases for solders are the three systems: Al-Si, Al-Ge and Al-Zn. The melting point of the Al-11, 7% Si eutectic is 578°C. The Al-Si alloys have a relatively high corrosion-resistance.

At present, binary Al-Si alloys, with or without impurities, are used as a base for many aluminum-solders.

A certain disadvantage of the Al-Si base solders arises from their blue-gray color (tint) as compared with the white color of aluminum and its copper-containing alloys. Moreover, Al-Si base alloys are unsuitable for anode-plating operations (at a Si-content higher than 3%).

In many respects, binary Al-Ge alloys are similar to Al-Si alloys (Germanium and silicon have many identical properties). The melting point of the Al-55% Ge eutectic is 423°C. Due to the scarcity and expensiveness of germanium these solders are of little use.

A series of Al-Zn alloys is used for soldering purposes. Zinc lowers the melting point of aluminum less than do silicon and germanium; so, for instance, to attain a solidus temperature of 600°C, 30% Zn should be added to aluminum. The Al-30% Zn alloys have low plasticity; therefore, to many aluminum alloys zinc is added in smaller quantities. Alloys with a pure-zinc content have a relatively high corrosion resistance. The corrosion resistance of Al-Zn alloys is considerably lowered by the presence of impurities.

In order to facilitate the selection of low-melting aluminum-base alloys for soldering alloys, a series of ternary eutectics have been tried. Table 31 presents composition of some ternary and quaternary aluminum-base eutectics. These data permit us to estimate the feasibility of reducing the melting point of aluminum alloys by alloying them with various constituents.

Most of the ternary and quaternary eutectics have low plasticity and are undeformable. It is known, however, that the eutectic containing 79.8% Al, 13.5% Si and 6.7% Mg, may be subjected to rolling operations [49].

Several ternary eutectics have been tested before their use as solders. Most of them are unsuitable for soldering aluminum and its alloys, due to a reduced plasticity and corrosion-resistance. For some soldering alloys it is still necessary to devise fluxes working at temperatures close to the melting point of the eutectic involved. This particularly applies to soldering of magnesium-bearing alloys or for the use of magnesium-bearing solders.

For soldering of aluminum alloys, a ternary Al-CuAl₂Si eutectic solder may be used with a melting point of 525°C [50/ 51]. This solder is known in the USSR under the name of 34A solder.

Some uncertainty exists still about the composition of the ternary Al—CuAl₂—Si eutectic, thus hindering the judicious blending of the solder.

Table 32 brings data on the composition of these solders according to various investigations

Table 31

Aluminum-base ternary and quaternary eutectics

Composition of eutectic, %								Melting point, °C
Al	Si	Cu	Mg	Ni	Mn	Fe	Zn	
86.8	12	—	—	—	1.2	—	—	570
84.3	11.8	—	—	3.9	—	—	—	568
87.0	12.5	—	—	—	—	0.5	—	557
82.06	12.97	—	4.97	—	—	—	—	550
67.2	—	32.5	—	—	—	0.3	—	542
67.4	—	29.6	—	—	3	—	—	538
68.9	—	28.6	—	2.5	—	—	—	532
63.5	5	31.5	—	—	—	—	—	525
66	—	1	33	—	—	—	—	449
65.25	0.75	—	34	—	—	—	—	448
65.5	—	1.5	33	—	—	—	—	445
71.25	—	—	26.5	—	—	2.25	—	437
43.6	—	—	26.4	—	—	—	30	478
43	—	—	43	—	—	—	14	448
63.1	—	29.7	7.2	—	—	—	—	501
65.5	—	1.5	33	—	—	—	—	445
64.8	4	28.1	3.1	—	—	—	—	505
62.8	0.45	29.6	7.15	—	—	—	—	505
65.3	0.3	1.5	32.9	—	—	—	—	444

Table 32

Composition of ternary Al-Cu-Si eutectics

Composition of eutectic, %			Source of information
Al	Cu	Si	
65.8	29	5.2	/52/
67.5	26	6.5	/52/
63.5	31.5	5.0	/53/

Table 33 presents some available aluminum-base solders.

Proposals have been made for the use of solders which contain about 30% Zn. For reclaiming of aluminum castings, a certain time, VPT-4 solders with 55% Al, 40% Zn and 5% Si have been used. Nearly all these solders (Except No. 9 and 10) are suitable for the soldering of aluminum and its high-melting alloys (AMts, AMg, AV etc.); they are unsuitable for soldering of duralumin (grade D1 and D16) since on heating it above 505°C a low-melting eutectic forms (the so-called burning effect), accompanied by an intense reduction of mechanical strength and plasticity. Burning of

duralumin may, in certain cases, be avoided by a rapid surface heating of the parts in a high-frequency induction furnace.

In an atmospheric environment and in water (even in sea-water) aluminum-soldered joints are corrosion proof but are unstable in alkalis and acids; therefore, aluminum-alloy vessels for nitric acids, should not be soldered with aluminum-base solders. Welded vessels have a better corrosion resistance.

Table 33

Aluminum-base solders

Composition of solder, %							Temperature °C			Source of information, grade of solder
Cd	Al	Si	Cu	Zn	Mn	Sn	Solidus	Liquidus	Soldering	
—	96—94	4—6	—	—	—	—	577	630	62—640	/54/
—	96—94	6.8—8.2	—	—	—	—	577	613	60—615	/54/
—	96—94	9.3—10.7	—	—	—	—	577	—	—	
—	96—94	11—13	—	—	—	—	577	582	578—640	/54/
—	86	10	4	—	—	—	521	583	570—640	/54/
—	89	1	10	—	—	—	540	625	—	/49/
—	80	—	—	20	—	—	575	620	—	
—	67.5—64.5	5.5—6.5	27—29	—	—	—	525	535	540	34A
—	52.2	3.5	20	24	0.3	—	—	470	495—505	/51/
—	51.2	3.5	25	20	0.3	—	—	480	495—505	B-62
—	61.2	3.5	20	15	0.3	—	—	500	500—530	Authors
15	63	7	10	—	—	5	—	550	570—600	
—	80—76	7—9	13—15	—	—	—	525	540	—	PA-1
—	72.5—71	7.5—8	20—21	—	—	—	525	537	—	PA-2
—	70—65.5	6—7.5	24—27	—	—	—	—	—	—	VPT-3

§ 10. Silver-Base Solders

The group of silver-base solders covers alloys in which one of the phases is formed by silver or by its solid solution. Silver-solders have been used since ancient times /55/. They are extensively employed for they possess the following properties: a relatively low melting-point, high mechanical-strength, good plasticity and machinability and finally, good corrosion resistance in various media.

Let us consider first the most commonly used silver-solders, classifying them according to their structural characteristics. Most of the silver solders contain copper and, as a rule, form eutectics upon crystallization. Copperless silver solders, represent in principle solid solutions. A group of silver solders is used for soldering copper and titanium parts, and covers

silver solders with 15% Mn, used in soldering of parts subjected to high temperatures (e.g. turbine blades etc.) These solders have a relatively high strength at elevated temperatures: the tensile strength is 15 kg/mm^2 at 850°C ; and $\sigma_v = 28 \text{ kg/mm}^2$ at 20°C ; $\sigma_{0.2} = 9 \text{ kg/mm}^2$; (for silver solders at 20°C , $\sigma_v = 15.7 \text{ kg/mm}^2$ and $\sigma_{0.2} = 3 \text{ kg/mm}^2$). The melting point of this solder is 976°C , its solid solution has a close to the maximum value ($\sim 20\% \text{ Mn}$). Among such solders, an alloy containing 75% Ag, 20% Pd and 5% Mn should be mentioned. Its melting point exceeds 1100°C . The shear strength amounts to 6.5 kg/mm^2 at 600°C , and 2.5 kg/mm^2 at 850°C /24/.

The following solid solutions or alloys may also be used: 1) Cu—Ag (13% Cu) with the liquidus at 805°C ; 2) Zn—Ag (25% Zn), with the liquidus at 710°C ; 3) Cd—Ag (25% Cd), with the melting range from 705 to 730°C /24/. These solders are little known. Several solders of the binary Ag—Cu system are listed in Table 34.

Table 34

Silver-copper solders

Composition of solder %		Temperature $^\circ\text{C}$			Specific gravity g/cm^3
Ag	Cu	solidus	liquidus	soldering	
72	28	778	778	778-900	9.9
67	33	778	805	805-900	9.8
50	50	778	850	850-950	9.3

Since these solders contain no elements evaporating during heating, they are suitable for soldering of vacuum-devices; their electric resistivity is low but can be improved by addition of zinc and cadmium.

The binary Ag—Cu eutectic has been used as a starting base for a series of more complex alloys. For this purpose the great solubility of Zn and Cd in Ag and Cu has been resorted to. The Ag—Cu eutectic has a spherulitic structure. Copper grows from one of the centers in the form of shoots (guiding phase) whereas silver fills in the remainder of the grain (guided phase) (Figure 31). The equilibrium diagrams of the binary Ag—Zn, Ag—Cd and Cu—Zn alloys show a similar structure: they contain isomorphic phases. Of practical importance are the soldering alloys containing plastic solid-solutions on the base of Ag or Cu.

In the presence of a brittle β -phase (AgZn, CuZn, AgCd or their liquid solution) with a centered crystalline structure of the CsCl type, the plasticity of the soldering alloy is very low. Despite the reduction of the liquidus temperature by adding a large quantity of Zn and Cd to these alloys, they did not find a wider use due to their reduced plasticity associated with the formation of a β -phase or the more brittle γ -phase.

Most studied are the soldering alloys of the Ag—Cu—Zn system, Figure 48, a, /57/ illustrates the phase composition of the equilibrium Ag—Cu—Zn alloys in the solid state. The liquidus regions of this system are given according to Leach /58/ in Figure 48 (b).

Table 35 presents some data on soldering alloys of the Ag—Cu—Zn system. In the equilibrium diagram of Ag—Cu—Zn, these alloys do not extend over the region of the presence of α_1 -, α_2 - or $(\alpha_1 + \alpha_2)$ -phases.

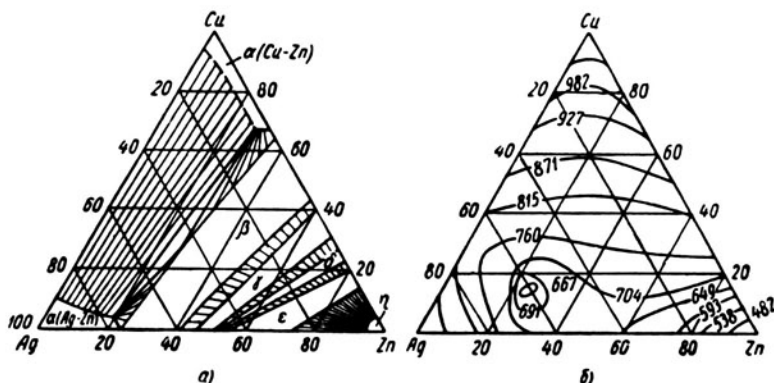


Figure 48. Phase composition (a) and surface (b) of the liquidus region in alloys of the Ag—Cu—Zn system (α , β , γ , δ , ϵ , η are phases of the system)

The ternary Ag—Cu—Zn alloys have been standardized in the USSR. Table 36 presents their chemical composition and some mechanical properties.

The use of these alloys is given in Table 37.

Table 38 gives the mechanical properties of some L62 brass solders and joints, soldered with silver solders /65/.

The presence of various impurities in the soldering have a great influence on the properties of the solders. With an Ag-content of up to 25%, the solders are allowed to include up to 1% impurities (among them up to 0.5% Pb); at a greater Ag-content, the total amount of impurities should not exceed 0.5 and 0.3% Pb. U.S. Standards allow for 0.15% impurities; the British allow 0.5%.

The solders of the Ag—Cu system with the lowest melting point contain Zn and Cd in a proportion close to that of the eutectic Ag—Cu (3:1). Partial replacement of zinc by cadmium in solders consisting of α_1 - and α_2 -phases, leads to an increase in the temperature of the liquidus. This is due to the fact that zinc causes a greater reduction of the liquidus of the solid solution of silver than cadmium. The solubility of cadmium in copper or in silver is insignificant as compared with that of zinc.

Solders of the Ag—Cu—Cd and Ag—Cu—Cd—Zn system. Tables 39 and 40 present a series of solders of this system, containing from 10 to 80% silver. Figure 49 shows four quaternary systems containing Ag, Cu, Cd, Zn /64/.

A study of the quaternary Ag—Cu—Cd—Zn system revealed the existence of alloys of a lower melting point and with sufficient plasticity. These alloys have two phases (solid solutions on a silver and copper base). Apparition of an intermetallic phase, connected with an excess quantity of Zn or Cd, leads to embrittlement of the solders.

The Ag—Cu—Cd—Zn system exhibits the best properties at a silver content of 40–50%; moreover, these solders have the lowest solidus point and a structure typical of the binary Ag—Cu eutectic with excess primary phases. Zinc and cadmium occur in these systems in the solid solution of

Ag and Cu. Figure 50 illustrates the typical temperature dependence of the crystallization range of the Ag-Cu-Cd-Zn solders with an Ag-Cu eutectic structure associated probably with an excess of the primary Ag and Cu solid solution without a β -phase /68/.

Table 35

Solders of the Ag-Cu-Zn system

Composition of solders, %			Tensile strength, kg/mm ²	Elongation, %	Temperature, °C, of:			Grade of Solder	Source of information
Ag	Cu	Zn			Solidus	Liquidus	Solidus		
7-9	55	Remainder	51	7	—	850	850	—	DiN 1734
9.7-10.3	52-54	»	—	—	810	850	870	PSr ₁₀	
11.7-12.3	35-37	»	—	—	750	800	820	PSr ₁₂	
11-13	52	»	54	31	—	820	820	—	DiN 1734
15	52	33	56	3	810	835	835	—	/59/
20	45	35	—	—	777	815	820	—	/60/
24.7-25.3	39-41	Remainder	—	—	745	775	780	ПСр-25	
24-26	43	»	50	10	—	770	770	—	DiN 1734
32	35	33	38.5	8	714	755	755	—	/59/
40	36	24	40	6	721	785	785	—	/60/
42-44	36-38	18.5-20.5	34.5	12	700	775	775	—	/6/
44.5-45.5	29.5-30.5	24.5-25.5	—	—	665	745	745-845	PSr ₄₅	/54/
43-45	32	Remainder	—	—	—	720	730	—	DiN 1734
50	34	16	—	—	690	775	775-870	—	/54/. /60/
50	28	22	—	—	675	727	—	—	61
59-61	28	Remainder	47	30	—	700	700	—	DiN 1735
60-62	27.5-29.5	9-11	39.5	16	695	735	—	—	/59/
60	25	15	46	34	695	720	720	—	/62/
60	15	25	53	28	674	677	680	—	/59/
65	15	20	—	—	—	720	720	—	/59/
64.5-65.5	19.5-20.5	14.5-15.5	—	—	695	720	720-845	PSr ₆₅	/60/
66-68	26	Remainder	—	—	—	720	720-755	—	DiN 1735
70	20	10	—	—	725	755	870	—	/54/
69.5-70.5	25.5-26.6	Remainder	—	—	730	755	760	PSr ₇₀	/59/
74	14	12	—	—	—	788	788-900	—	/54/
75	22	3	—	—	740	—	—	—	
80	16	4	—	—	738	793	—	—	/62/
82-84	16-18	—	—	—	—	—	830	—	—

In the crystallization range of these solders, three critical points have been detected. This is due to the peculiarities of the equilibrium diagram, in which the two components, Ag and Cu, form a simple binary eutectic in combination with the Ag-Zn, Ag-Cd or the Cu-Zn peritectic groups. Typical cross-sections of quasi-binary Cu-Zn systems with 50% Ag are given in Figure 51 /64/.

Ternary and quaternary silver solders containing tin, nickel, or manganese. Some silver solders, apart from Cu, Zn and Cd contain other constituents (Sn, Mn and Ni). The effect of tin in silver solders is similar to that of Cd or Zn.

Properties and composition of standard silver solders Table 36

Grade of solder	Composition of solder, %			Maximum quantity of impurities		Specific gravity g/cm ³	Temperature, °C		Tensile strength, kg/mm ²	Electric conductivity in % of pure copper
	Cu	Ag	Zn	Pb	Total		Solidus	Liquidus		
PSr10	50±1	10±0.3	Re-mainder	0.5	1	8.6	815	850	—	6.5
PSr12	36±1	12±0.3	Same	0.5	1	8.5	750	800	18.5	11.1
PSr25	40±1	25±0.3	»	0.5	1	8.9	745	775	28	6.9
PSr45	30±0.5	45±0.3	»	0.3	0.5	9.3	600	725	30	9.7
PSr65	20±0.5	65±0.5	»	0.3	0.5	9.6	685	720	30—35	8.6
PSr70	26±0.5	70±6.5	»	0.3	0.5	9.8	730	755	30—35	4.2

Table 37

Applications of silver solders

Grade of solder	Base metal and alloys	Application of solder
PSr10	Copper, copper alloys, steel	Soldering steel and nonferrous metals, soldering copper on steel
PSr12	Brass containing 58 % Cu	Soldering of brass and copper parts
PSr25	Copper and its alloys, steel	Soldering parts requiring a neat seam and elevated strength under shocks and vibration
PSr45	Copper, brass, stainless steel	Soldering parts requiring a neat seam and elevated resistance to shocks and vibrations; soldering of electro-technical equipment
PSr65	Steel	Soldering of band saws, of small parts and food-vessels
PSr70	Copper, brass, silver	Soldering of conductors or their parts of an elevated electric conductivity

Table 38

Tensile strength of cast solders and of soldered L62-brass joints

Grade of solder	Tensile strength kg/mm ²	Shear strength kg/mm ²
PSr12	19.3	20
PSr25	23	25.5
PSr45	32	28.5

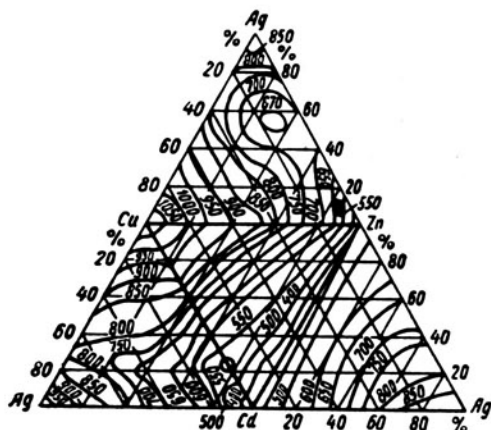


Figure 49. The surface of the liquidus of the quaternary system Ag-Cu-Zn-Cd

Since the solubility of Sn in Ag and Cu is much smaller than in Cd or Zn, tin is added to silver solders in relatively small quantities. Besides, unlike Zn and Cd, tin has a small vapor pressure (tension); therefore, as distinct from the Ag-Cu-Zn-Cd solders, Ag-Cu-Sn solders may be used also in soldering of vacuum-devices.

The content of Zn or Cd in solders required for soldering of vacuum devices should not exceed 0.005 %.

Although investigations still failed to reveal completely the action of nickel in silver solders, nickel is known to increase the wetting power of molten solders and the rate of their inflow into the gap between the parts. Nickel is immiscible with silver but it forms with copper continuous series of solid solutions; therefore, nickel can be added to solders only in the presence of copper; its addition leads to brightening of the solder. By addition of nickel, the liquidus temperature of silver solders is greatly increased. In order to lower the liquidus point of such solders, manganese, also being a good deoxidant, may be added.

Nickel increases the strength of the solder but has little influence on its plasticity.

Thanks to nickel-bearing silver solders used for soldering nickelless steels, corrosion in the interface between the steel and the solder can be avoided; this is due to the formation of thin interlayers of nickel between the base metal and the solder (see Figure 52) /69/.

Table 41 brings some silver solders containing Sn, Ni and Mn.

Solders of the Ag-Cu-Cd-Zn system

Composition of solder, %				Temperature of liquidus, °C	Source of information
Ag	Cu	Cd	Zn		
10	40	10	40	777	/24/
11-13	52	5-9	32-26	790	DIN 1734
14-16	49	8-12	29-23	760	DIN 1734
19-21	43	13-17	25-19	740	DIN 1734
20	30	20	30	735	/24/
49-51	32	3-7	16-10	690	DIN 1734
49-51	22	16-20	13-7	640	DIN 1735
58	25	14	3	691	/56/
65	20	2.5	12.5	719	/24/, /2/
65	20	6	9	730	/24/, /2/
65	20	10	5	743	/24/, /2/
65	20	15	—	752	/24/, /2/
66-68	13	11	10-8	700	DIN 1735
75	15	5	5	748	/56/
75	20	5	—	775	/60/
80	16	4	—	810	/60/

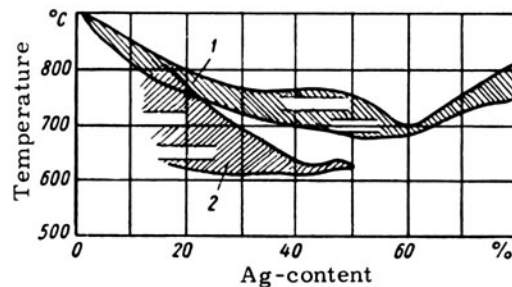


Figure 50. Temperature region of crystallization in applied silver solders:

- 1) Ternary solders; 2) Quaternary solders (Brooker, Batson).

In the following, several data are given to show the influence of a gradual widening of the composition of silver solders on their technological properties. The melting point of silver is 961°C . By addition of copper, the solidus can be lowered to 778°C . In the Ag-Cu-Zn alloys used for soldering purposes, the solidus temperature is 680°C . In the quaternary relatively plastic Ag-Cu-Zn-Cd system, based on the $\alpha_1 + \alpha_2$ eutectic, the minimum solidus temperature is $\sim 600^{\circ}\text{C}$.

Table 40

Solders of the quaternary Ag-Cu-Cd-Zn system

Composition of solder, %					Temperature, °C		Tensile strength (cast state), kg/mm ²	Source of information	Grade of solder
Ag	Cu	Cd	Zn	Ni	Solidus	Liquidus			
11.5—12.5 20	49—50 45	3—4 5	34—37 30	—	805 777	825—900 815—900	—	—	—
29—31 35	19—21 26	20—25 18	20—25 21	—	605 607	685—850 700—845	37.0	/55/ /59/ /54/ /65/ /61/	—
38—42 40	16—20 18	22.5—26 27	13.5—12 15	—	—	<650 650—750	—	TUTsMO 1078-55[66]	PSr-40
39.1—41.1 40—43 40	15.5—16.5 16—20 20	25.1—26.5 28—17 20	17.3—18.5 16—20 20	0.1—0.3 —	613 600 608	605 621 650	38—44 45	/59/ /54/ /67/	—
44.5—45.5 44—46 49—51	14.7—15.3 19 14—16	23.5—24.5 18—22 18—20	15.5—16.5 19—13 19—13	—	607 610 630	618—760 620 ≥620 640—760	—	VTUTsMO 1032-54 DIN 1734 /59/	PSr-45 —

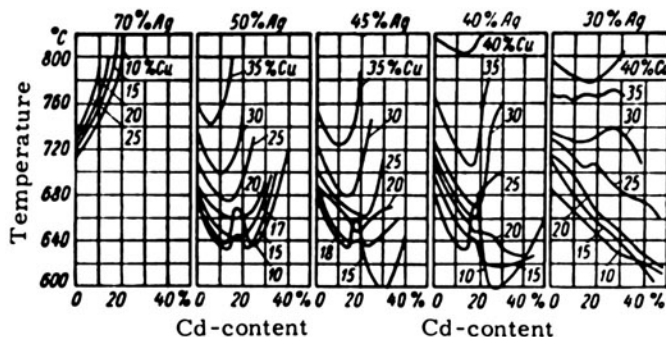


Figure 51. The liquidus temperature of ternary Ag—Cu—Cd systems in quasi-binary cross-sections, at a constant silver content

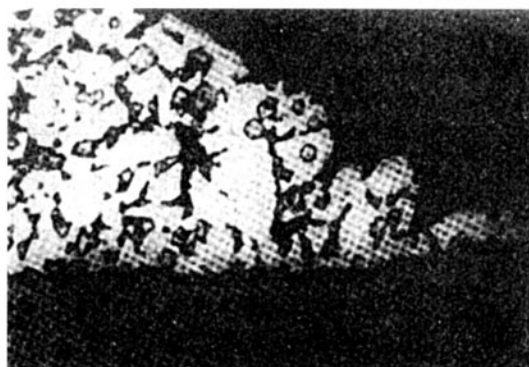


Figure 52. Microstructure of stainless steel joints soldered with nickel-containing silver solders

In Ag—Cu—Zn soldering alloys, a relatively high fluidity and flowability (in the gap) of the molten solder can be obtained at an Ag-content of ~ 60%; in the case of quaternary Ag—Cu—Zn—Cd soldering alloys, this can be done by adding ~ 42-45% Ag. A reduction of the silver content below ~ 40% in these solders causes an increase in the crystallization range as well as an appearance of brittle phases which leads to a deterioration of the technological properties and finally to a poor quality of the soldered joint.

For soldering copper and its alloys, another eutectic is used, a ternary one based on the Cu—P—Ag system. This eutectic has three phases: Cu, Ag, and Cu_3P (17.9% Ag, 30.4% Cu and 51.7% Cu_3P). The per-cent composition of the eutectic is: 74.9% Cu, 17.9% Ag and 7.2% P; the melting point is 646°C. Solders with a smaller silver content than the Ag—Cu—P eutectic

are also used. Table 42 presents some data on these solders (and on solders of the Cu-P type) according to the AWS.

Table 41

Multicomponent, tin-, nickel-, and manganese-bearing silver solders

Composition of solder, %								Temperature, °C		Remarks
Ag	Cu	Cd	Zn	Sn	Ni	Mn	Si	Solidus	Liquidus	
26—28	40	—	16—18	—	6	10	—	—	830	DIN 1734
38	42	—	16	4	—	—	—	—	800	DIN 1734
40	30	—	28	—	2	—	—	670	780	—
40	19.5	20.5	14	—	—	6	—	—	716	/56/
46.5	32.5	—	—	21	—	—	—	600	640	—
48—50	18	—	19—21	5	8	—	—	—	680	DIN 1734
48—50	12.2—	25.3—	14.4—	0.5—	—	—	0.05—	—	—	PSr 48 _{KH}
	13.2	26.7	12.6	0.9	—	—	0.15	—	700	—
53	32	—	—	15	—	—	—	670	690	/8/
50	15.5	16	15.5	—	3	—	—	645	800	—
43	37	—	—	3	2	15	—	—	650	—
56	22	—	17	5	—	—	—	620	670	DIN 1735
59—61	25	3	8—10	3	—	—	—	—	720	—
60	30	—	—	10	—	—	—	590	785	—
65	28	—	—	—	2	5	—	750	755	—
68	27	—	—	5	—	—	—	730	842	—
80	5	8	2	5	—	—	—	—	770	—
80	2	—	13	5	—	—	—	—	—	—
49—51	14.5—	15—17	13.5—	—	2.5—	—	—	640	648	ASTM, BAg3
	15.5	—	17.5	—	3.5	—	—	—	—	—

These alloys display a tendency to liquation; therefore, the crystallization rate during soldering should be as high as possible. The corrosion resistance of these solders in various media is satisfactory; however, they should not be used in soldering of joints which are working in an air or gaseous (sulphur) environment, at temperatures above 20°C.

Addition of silver to Cu-P solders increases the mechanical strength of the soldered joints (see table 43) /63/.

Table 42

Copper-phosphorus silver and silverless solders

Composition of solders, %			Temperature, °C, of		
Cu	P	Ag	Solidus	Liquidus	Soldering
95.25—94.75	4.75—5.25	—	707	900	790—930
93.25—92.5	6.75—7.50	—	707	817	730—845
89.25—88.25	6.00—6.50	4.75—5.25	646	815	650—845
87.5—85.95	6.75—7.80	5.75—6.25	640	750	650—815
80.25—79.75	4.75—5.25	14.50—15.50	640	815	650—815

Table 43

Tensile strength of L62-brass joints, soldered with silver-bearing copper-phosphorus solders

Composition of solder, %			Temperature, °C	
Cu	P	Ag	Tensile strength kg/mm ²	Shear strength kg/mm ²
92.5	7.5	-	16.5	28.9
99.5	5.2	2.3	19.4	33.4
89.6	5.5	4.9	21.3	36.9
80.2	4.8	15.0	27.5	41.1

Authorities differ about the exact data on the mechanical strength of joints soldered with copper-phosphorous solders; this may be explained by a varying quality of the starting (charging) materials.

Table 44

Relation between the strength of low carbon-steel joints soldered with ternary and quaternary silver solders, and the temperature /59/

Composition of solder %	Test temperature °C	Tensile strength kg/mm ²	Composition of solder %	Test temperature °C	Tensile strength kg/mm ²
50 % Ag and 15 % Cu; 16 % Zn and 19 % Cd	20	30	25 % Ag and the remain- der Cu and Zn	20	26
	100	29		100	25
	200	28		200	24
	300	27		300	23
	400	23		400	22
	500	9		500	20

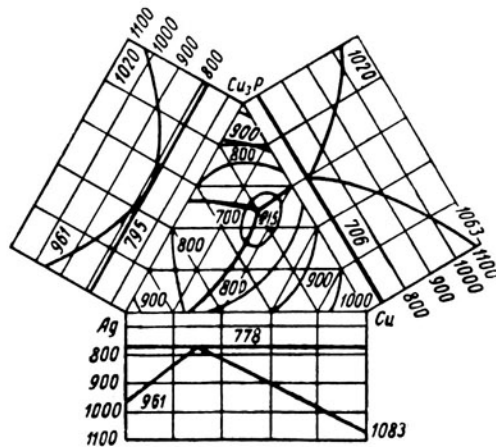


Figure 53. Ternary equilibrium diagram of the Ag-Cu-Cu₃P system (according to Frölich)

Fig 53 presents the ternary equilibrium diagram of the Ag-Cu-P system /70/. Some data on the influence of the phosphorus content on the copper-silver solders may be found in the bibliography /71/ and /72/.

Silver solders have a relatively reduced heat resistance. The heat resistance of ternary Ag-Cu-Zn solders is higher than that of the quaternary Ag-Cu-Zn-Cd cadmium-bearing solders. Table 44 affords some idea of the variation of the strength of two groups of silver solders with the temperature.

The heat resistance of quaternary solders at temperatures higher than 500°C suffers a sudden reduction whereas ternary solders remain rather resistant at these temperatures.

§ 11. Copper-Base Solders

Copper solders are used for the soldering of steel, tungsten, molybdenum, nickel and nickel-alloy parts, particularly in furnaces with a reducing atmosphere or in high-frequency induction furnaces. For soldering purposes, deoxidized copper with a smaller impurity content may also be suitable. As deoxidants silicon, phosphorus (in amounts up to 0.05% that do not induce a brittle layer in steel joints), and particularly lithium may be used.

A series of elements form with copper alloys whose melting points are lower than that of pure copper (e.g., Zn, Ag, Sn, Mn, and P). Constituents like Fe and Ni are added to copper alloys, particularly for elevating the melting point. The most commonly used copper-base solders are the following: Cu-Zn, Cu-Ag, Cu-P, and Cu-Ni. The binary Cu-Ag and Cu-P alloys form low-melting eutectics. The binary Cu-Ni alloys form a continuous series of solid solutions.

The wide use of brass solder for soldering of copper alloys is due to the relatively low melting-point, the narrow crystallization range and the solubility of zinc in copper. The liquidus point of brass steadily lowers with the increase in the zinc content. The Cu-Zn alloys possess several inter-metallic phases formed upon crystallization in a peritectic reaction. Brasses with a zinc content of up to 39%, (and no less than 61% Cu), in the equilibrium condition consist of the solid solution of Zn in Cu (the α -phase). In alloys with 39-50% Zn, a β -phase is formed (on the base of the CuZn compound). Apart from the β -phase, in alloys with 50-60% Zn, a γ -phase is formed (on the base of the Cu_5Zn_8 compound).

Table 45

Mechanical strength of cast brasses

Cu-content of brasses %	Tensile strength σ_v kg/mm ²	Elongation δ %	Phase composition
85	23	34	α
62	32	40	α
60	40	35	$\alpha + \beta$
54	26	5	$\beta + \alpha$
48	17-21	3	$\beta + \gamma$
42	4	0-2	γ

The mechanical strength of cast brasses composed of an α -phase, steadily grows with the increase in the zinc content (Table 45).

Formation of the β -phase, besides the α -phase, increases the mechanical strength but lowers the plasticity; the γ -phase is very brittle; therefore, brass containing such a phase has reduced strength and plasticity. Solders containing the β - and especially the γ -phase, in spite of their relatively reduced strength, are used in soldering some types of copper-alloys due to their low melting point. Due to their brittleness, alloys with a copper content below 42 % are unsuitable for soldering purposes.

Some properties of brass solders (according to DIN 1733) are given in Table 46.

Table 46

Brass solders¹ (according to DIN 1733)

Copper content of solder, %	Temperature of, °C			Specific gravity g/cm ³	Color
	Solidus	Liquidus	Soldering		
84-86	1005	1025	1020	8.7	Golden yellow
62-64	900	910	910	8.4	Bright yellow
59-61	890	900	900	8.4	Darker than a Cu 63 % alloy
53-55	880	885	890	8.3	Golden yellow
47-49	855	865	870	8.2	Straw yellow
41-43	830	840	845	8.1	Grayish ²

¹ These solders contain 0.2-0.4 % Sn
² The γ -phase has a gray color

In the USSR, only three copper-zinc solders have been standardized. Most extensively used are the L62 and L68 brass solders.

Due to its brittleness, the PMts-36 solder has but little practical use. The solders of the PMts-48 and PMts-54 type are used for soldering joints not subjected to shock, bending or vibration stresses. The L62 and L68 brass solders are employed in joints which are in a relatively stressed condition and require a high degree of plasticity. (Table 47).

The British Standard 1845 for copper-zinc alloys covers alloys containing 50.54 % and 60 % Cu. This standard also covers brass solders with a content of 1 % Sn, with 54 and 60 % Cu. The melting point of these solders differs by 5-10 % from that of alloys with the same Cu-content. These alloys are prone to form porous joints (with "voids"). Tin, however, increases the corrosion resistance of brasses in sea water. Addition of tin to L62 brass improves its spreadability. Due to their reduced plasticity tin-bearing brass solders have found no wider use.

The basic disadvantage of brass solders is the partial evaporation of zinc during soldering owing to the high pressure of the zinc vapors. Pure zinc boils at 906°C. In brass, the evaporation temperature of zinc increases and attains value of 1000°C at a Cu-content of 50 %, a value of 1200°C at a Cu-content 75 % and a value of 1400°C, at a Cu-content of 85 %. During evaporation of the zinc from the brass alloys, a white zinc-oxide (ZnO) is formed with a melting point of 1975°C. The temperature of evaporation of zinc from brass alloys differs from that of brass only by 100-200°C.

Overheating of brass solders during the soldering process is therefore highly undesirable, since it lowers the properties of the soldered joints (inducing porosity). Zinc-oxide vapors are poisonous and cause fever phenomena.

Table 47

Copper-zinc solders

Grade of solder	Composition of solder, %			Temperature, °C		Tensile strength, kg/mm ²	Elongation, %	Applications
	Cu	Pb	Fe	Solidus	Liquidus			
PMts-36	35—37	≤ 0.5	0.1	800	825	3	0—1	For soldering brass with a Cu-content up to 68% For soldering copper alloys containing 62% Cu
PMts-48	47—49	≤ 0.5	0.1	860	870	21	3	
PMts-54	53—55	≤ 0.5	0.1	870	880	26	5	
L62	60.5—63.5	≤ 0.08	0.15	900	905	31	38	For soldering copper, tombac, bronze, alpaca
L68	67—70	≤ 0.09	0.10	—	940	30	40	For soldering copper, steel, nickel, cast iron The same

During heating the solders tend to absorb hydrogen which causes (a general or even intercrystalline) brittleness; therefore, soldering of brass base-metals should not be performed with a reducing but an oxidant flame. The latter partially prevents evaporation of zinc in brass solders.

By adding a quantity of 0.1-0.5 % silicon, the evaporation of zinc in brass can be appreciably reduced. Silicon impedes diffusion of zinc and lowers the solubility of hydrogen in brass alloys, i. e., it reduces the dangerous (harmful) formation of porosity during crystallization.

It is also supposed that in an oxidant gas-flame a layer (probably of Zn and SiO₂) is formed, that is impenetrable to zinc and is dissolved in the flux.

According to another hypothesis, during the melting of the solder, zinc forms together with the atmosphere's oxygen and with the boron of the flux, boron-silicates, which, floating on the surface of the bath protect the zinc in the molten brass from oxidation and evaporation /24/. Probably both modes of action of Si on the properties of molten brass seem to be present.

The reduction of porosity of silicon-containing copper-zinc alloys, leads to an increase in their mechanical strength. According to some researchers, the porosity in brass is not connected with evaporation of zinc but with an evolution of gases (mainly hydrogen) /73/, /74/.

Silicon and tin visibly lower the solubility of zinc in copper; therefore, their addition to the solder increase the amount of the β -phase.

G. A. Asinovskaya proposed two tin-and silicon-bearing solders.

1) LOK62-06-04, containing 60-63 % Cu, 0.3-0.4 % Sn and 0.4-0.6 % Si;

2) LOK59-1-03, containing 58-60 % Cu, 0.7-1.1 % Sn and 0.2-0.4 % Si /63/. The melting point of both solders is $\sim 950^{\circ}\text{C}$. The specific gravity of these solders is greater than that of the L62 solder; they are used for soldering of joints working under a hydrostatic pressure. The shear and tensile strength of St 3 steel joints soldered with the L62 and LOK62-06-04 solders is nearly the same ($\sigma_v \sim 43 \text{ kg/mm}^2$ and $\tau_{\text{shear}} = 30 \text{ kg/mm}^2$).

Addition of 1 % Ag and 0.2-0.5 % Si to bi-phase brasses increases their strength, plasticity (Table 48), fluidity and corrosion resistance.

Table 48

Influence of small additions of Ag and Si on the tensile strength and plasticity of cast brasses /75/

Composition of brasses, %				Tensile strength, kg/mm ²	Elongation, %	Crystallization range, $^{\circ}\text{C}$
Cu	Zn	Ag	Si			
59-61	41-39	—	—	33.0	24	890-900
59-61	39.8-37.5	1	0.2-0.5	43.8	43	893-896

By addition of phosphorous an appreciable reduction of the melting point of copper may be obtained. At a content of 8.25 % P, a eutectic (Cu-P) is formed with a melting point of 707°C . Cu-P alloys have a high fluidity; thanks to their technological properties they proved to be very suitable for soldering purposes. Their disadvantage consists in a relatively low plasticity, which makes them unsuitable for soldering of joints subjected to considerable bend and shock stresses or to cold-working; on the other hand, they may be used for soldering joints stressed in compression or tension. Copper-phosphorus solders are adequate for soldering of copper and copper-alloyed base-metals.

As usually indicated in hand books on soldering steel and nickel-alloys should not be soldered with phosphorous solders. The results of recent investigations do however allow us to draw conclusions regarding the feasibility of such a soldering process /76/-/78/, provided that the soldering temperature of steel and nickel-alloys be higher (up to 745°C in soldering steel and up to 795°C in soldering nickel joints) than the soldering temperature of pure copper-solders. When soldering with such solders, the common borax and boric anhydride fluxes should be replaced by a flux of the following composition: 56 % potassium fluoroborate, 36 % potassium metaborate and 8 % boric anhydride.

The mechanical strength of steel and nickel butt joints soldered with copper-phosphorus solders is considerably smaller (14 kg/mm^2) than of the solder itself; this fact is connected with the apparition of a brittle layer of iron or nickel phosphides during soldering.

In some instances, soldering steel with Cu-P solders may be accomplished in a reducing atmosphere.

Copper-phosphorus solders contain 4-8 % phosphorous /79/. Apart from the reduced fusibility and self-fluxing ability in soldering copper joints, these solders have a good deformability under pressure, at $450-650^{\circ}\text{C}$, which permits them to be drawn into thin strips or wire.

In the USSR, copper-phosphorus solders are used in the form of intermediate alloys (MF-1, MF-2 and MF-3); these alloys are added as deoxidizers of copper and its alloys and as blending components to the charge of solders which include copper in their composition.

In the cast form eutectic phosphorous copper (8 % P) has a tensile strength of about 33 kg/mm² and an elongation smaller than 1 %. At a temperature range of 500-600°C, this alloy may be subjected to plastic deformation and can be hot-drawn into wire of 1.5-2.0 in gauge. Semifinished mold-cast stocks may be forged at ~ 600°C into thin strips or be rolled into strips of 0.5 mm thick /85/. The electrical resistivity of the Cu-8 %P solder is 0.892 ohm/mm²/m.

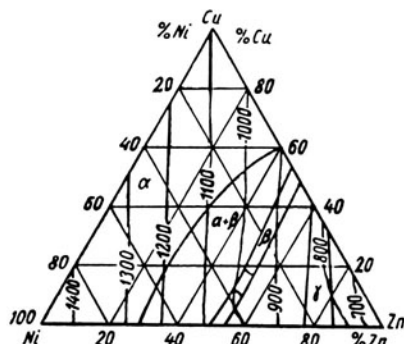


Figure 54. Temperatures of incipient crystallization and the phase composition of Ni-Cu-Zn soldering alloys (the three phases of the alloy are α , β , γ)

Butt soldering of some copper alloys (L62-brass, German silver, aluminum-bronze and copper-nickel alloys), with a Cu-8 % P solder, requires the use of a flux. The tensile strength of such joints is quite the same as of the cast solder (i. e., 33-34 kg/mm²). A soldered joint of good quality may be achieved by using a three-component flux of the following composition: 56 % potassium fluoborate (KBF₄), 36 % potassium metaborate (KBO₂) and 8 % boric anhydride (B₂O₃). The soldering temperature is 725°C.

Copper joints butt-soldered with a eutectic Cu-8 % P solder have a tensile strength of 20 kg/mm².

Soldering may be done without flux but at a temperature slightly higher than in the case of flux-soldering (730° instead of 716°C) /77/. In fluxless soldering, phosphorus is partially eliminated and in the structure of the soldered seam an excess phase of copper can be noticed.

The melting point of Cu-P alloys may be reduced by adding to them other constituents. Two such solders may be mentioned: one containing 58-66 % Cu, 5 % P, 1 % Sn and the remainder, zinc; this alloy has a lower brittleness than the Cu-8 % P alloys and melts at 670°C. The other alloy contains 6-7 % P, 2.5-3.5 % Sn, 1-3 % Zn and the remainder, copper (PFOTs 7-3-2). Its crystallization temperature ranges from 680° to 700°C and the melting point, from 730 to 750°C.

Table 49 brings the strength of copper and brass joints soldered with copper-phosphorus solders.

Table 49

**Strength of copper and brass joints soldered with
copper-phosphorus solders**

Composition or grade of solder	The base metals to be soldered	Tensile strength in kg/mm ²	
		of butt-joints	of lap joints
8 % Cu	Brass to brass	18-22	8-11
PFOTs7-3-2	Copper to copper	15-19	19-22
PFOTs7-3-2	Copper to brass	18-22	21-23
PFOTs7-3-2	Brass to brass	17-21	32-34

Table 50

German-silver solders

Composition of solders, %				Tensile strength, kg/mm ²	Remarks
Cu	Zn	Ni	Si		
53	33	14	-	40	/16/
43.5	38	18.5	-	37	/16/
41	42.5	16.5	-	30	/16/
38	50	12	-	14	/16/
35	57	8	-	9.5	/16/
> 45	> 40	6.11	0.2-0.4	-	DIN 1733
0-53	41-47.8	2-5	0.2-1.0	-	/24/
64	11	25	-	-	/24/
48	42	10	-	-	-
47	41.5	10.5	1 %	-	-
65	30	5	-	-	L65N

According to other data /83/, a tensile strength of 12-14 kg/mm² can be attained in butt soldering of copper, L62-brass and also of copper to brass with Cu-7% P and Cu-9 % P solders prepared by adding to them the intermediate alloys MF1, MF2 and MF3.

Table 51

Manganese-bearing copper solders

Composition of solders, %			Temperature of liquidus, °C	Tensile strength, kg/mm ²	Remarks
Cu	Zn	Mn			
67	12	22	683	40	/86/
64	20	16	869	34	/86/
61.4	32	6.6	898	34	/86/
58	29	13	845	46	/86/
99.5-97	-	0.5-3.0	-	-	/24/
85.25-83.75	0.25 Si	14.5-16.0	-	-	*

* Not more than 0.3 % Fe and 0.02 % Si.

Certain other alloys e.g., the ternary system Cu-Zn-Ni (German silver) and Cu-Zn-Mn, have also been proposed as solders. Some data on German-silver solders may be found in Table 50 and Fig 54.

These alloys have a binary structure (containing $\alpha + \beta$ -phases). Addition of silicon (as in the case of brass) reduces the evaporation of zinc during soldering.

Addition of manganese to copper or to copper-zinc alloys yields increased strength and plasticity (in some alloys). A series of such soldering alloys is presented in Table 51.

The solder No 5 is used in soldering of sintered hard alloys.

For soldering (or surfacing) of parts working at high temperatures and of those subjected particularly to friction (e.g., valves, etc), copper solders are used containing 2.5-10 % Fe with a liquidus range from 1180 to 1230°C or 20-30 % Ni with a liquidus range from 1200 to 1230°C. Solders having 75 % Cu and 25 % Ni are also suitable for soldering of tungsten or molybdenum parts.

Soldering of acid-proof steel parts is performed with solders containing 19-20 % Ni, 5-6 % Fe, 4.5-5 % Si, and the remainder Cu. The liquidus temperature extends over a range from 950° to 970°C.

Table 52

Bi-phase alloys for soldering cutting edges
to their tool-holders /87/, /88/

Grade of solder	Composition of solder, %							Temperature of	
	Cu	Zn	Fe	Ni	Mn	Zn	Si	Solidus, °C	Liquidus, °C
GPF	66-72	-	12-14	10-14	4.2-5.0	-	1.0-1.8	1190	1280
GPF	71-62	6-8	5-7	4-5	5-6	6-8	3-4	935	955

For soldering high-speed steel cutting edges to their holders, a two-phase copper-base solder is used (grade GPF); soldering of refractory hard alloy cutting edges is performed with GFK-solders (see Table 52) /87/, /88/.

Table 53

Tin-containing brass solders /54/

Composition of solder, %						Temperature, °C, of:		
Cu	Zn	Sn	Mn	Ni	Fe	Solidus	Liquidus	Soldering
57	42	1	-	-	-	890	900	915-955
56	40	1	1	1	1	870	890	915-955
51.5	45	3.5	-	-	-	860	875	880-930

These alloys consist of two solid solutions: on a copper base and on a Fe-Ni-Mn base.

For soldering of austenitic stainless-steel parts in a hydrogen atmosphere a special solder has been devised composed of 85 % Cu, 10 % Ni and 5 % Fe /89/.

The U. S. Standards for soldering alloys cover brasses with a small tin content (see Table 53).

Among the copper-base solders which contain no volatile elements (Cd, Zn) of great interest are solders of the Cu-Mn-Ni-Si system. Most interesting is the solder containing up to 15 % Mn, 30 % Ni and 1-2 % Si. The presence of manganese and silicon in these solders lowers the liquidus temperature whereas nickel raises this temperature. The temperature of the liquidus varies, depending on the composition of the solder, within the limits of 900-1130°C.

Addition of nickel, and to a lesser extent, of manganese, improves wettability and hardening of these solders, particularly at elevated temperatures; silicon improves their spreadability. All the three mentioned elements increase the corrosion resistance of the soldering alloys.

Of the above mentioned systems of solders, most commonly used are two types: 1) with 85 % Cu and 15 % Mn; 2) with 83 % Cu, 15 % Ni and 2 % Si. The first of these types is used for soldering structural steels, the second, for soldering stainless austenitic steels. Depending upon the required soldering temperature and the strength of the finished joint, the Ni-content may be raised up to 30 %.

The tensile strength of the second solder (in the temperature range from 200 to 600°C) varies within the limits of 15-30 kg/mm²; at a higher Ni-content it varies within the limits of 35-50 kg/mm².

§ 12. Gold-Bearing Solders

Gold and gold-rich solders have been in use since ancient times in the manufacture of various decorative works; later they have been used in

Table 55

Solders required for soldering vacuum equipment,
/29/, /92/

Composition of solders, %				Temperature, °C, of:		
Au	Cu	Ni	Ag	Solidus	Liquidus	Soldering
37.5	62.5	—	—	957	990	990-1100
30	70	—	—	—	1010	—
81.5	18.5	—	—	—	880	—
82.5	—	17.5	—	950	950	—
80	20	—	—	890	890	—
41.7	55.5	—	2.8	—	963	—
80	20	—	—	883	887	890-1010

Gold-bearing solders /24/, /90/, /91/

Composition of solders, %							Temperature of	
Au	Ag	Cu	Pd	Cd	Zn	Sn	Solidus, °C	Liquidus, °C
On an 18-carat gold base								
75	7.5	17.5	—	—	—	—	880	895
75	12	8	—	5	—	—	826	887
75	9	6	—	10	—	—	776	843
75	9	6	—	—	10	—	730	783
75	—	15	—	8.2	1.8	—	793	822
75	2.8	11.2	—	9	2	—	738	760
75	2.8	11.2	—	2	9	—	747	788
75	7.5	7.5	—	7	3	—	—	800
75	10	5	—	10	—	—	—	900
On a 14-carat gold base								
58.5	20	21.5	—	—	—	—	827	845
58.5	10.3	24.2	—	7	—	—	792	831
58.5	8.8	22.7	—	10	—	—	751	780
58.5	24.2	10.3	—	7	—	—	789	822
58.5	22.7	8.8	—	10	—	—	752	813
58.5	25	12.5	—	4	—	—	788	840
58.5	23.5	12.0	—	6	—	—	771	829
58.5	11.8	25.7	—	—	4	—	816	854
58.5	10.3	24.2	—	—	7	—	804	836
58.5	25.7	11.8	—	—	4	—	786	818
58.5	24.2	10.3	—	—	7	—	765	808
58.5	4.9	25.6	—	9	2	—	738	760
58.5	4.9	25.6	—	2	9	—	790	837
58.5	—	29.5	—	9.8	2.2	—	748	793
58.5	8	22	—	9.4	2.1	—	744	776
On an 8-carat gold base								
33.3	40	26.7	—	—	—	—	780	780
33.3	35	21.7	—	10	—	—	710	741
33.3	30	16.7	—	20	—	—	635	709
33.3	35	21.7	—	—	10	—	725	759
33.3	30	16.7	—	—	20	—	695	704
33.3	1.8	49.4	—	10.2	2.3	3	689	776
33.3	40.5	17	—	2.6	6.6	—	722	749
55	12	15	8	10	—	—	795	875
55	12	15	10	6	2	—	825	910
55	11	15	10	8	1	—	830	900
55	10	12	8	14	1	—	750	835
65	2	13	5	14	1	—	720	795
70	6	10	5	8	1	—	780	885
70	10	5	5	9	1	—	790	925
48	16	20	5	10	1	—	700	800
37.5	20	20.5	3	18	1	—	630	695

dentistry. Sometimes gold solders are required for soldering vacuum equipment. Certain gold-rich solders are listed in Table 54.

The inclusion of palladium in the composition of gold solders increases their corrosion resistance.

In the vacuum technique, gold bearing solders have been suggested also for soldering copper and iron to alloys of the Fe-Ni-Co group (Table 55)

§ 13. Nickel-Base Solders

Nickel has a high melting point (1452°C) and its solders are suitable for soldering alloys subjected to high temperatures and also for soldering alloys with a very high melting-point. Pure nickel is sometimes used for soldering molybdenum and tungsten; nickel may be adequate for soldering chromium and other elements with a high melting-point. Nickel is also used to form an intermediate layer e.g., when metals are soldered to a ceramic base.

The melting point of nickel may be lowered by addition of elements forming with nickel, eutectics, peritectics or low-melting solid solutions.

The following elements form relatively low-melting eutectics with nickel: S, Sb, Sn, Si, C, Cr, B, Be, Mn, Zn, and P. The first three of these elements are liable to cause embrittlement of nickel alloys; therefore, their addition to these solders is inadequate. Eutectic solders containing 89 % Ni and 11 % P and melting at 880°C , are used in the diffusion soldering of nickel alloys.

The melting point of Ni-Si eutectics (with $\sim 10\%$ Si) is 1150°C . Silicon exerts a visible embrittling action on nickel even when added only in small quantities; however, nickel is included in the composition of some solders. Silicon is dissolved by nickel, up to $\sim 6\%$.

Until now the carbon content of the Ni-C eutectic could not be exactly determined (it contains 2.2 % C at 1315°C). Carbides are formed in the presence of carburizing elements in these alloys. At a content of $\sim 50\%$ Cr and at 1320°C , a Ni-Cr eutectic is formed. Nickel contains up to $\sim 30\%$ dissolved chromium. In nickel-alloys, chromium constitutes an important hardener and the basic element for satisfactory heat resistance. Nickel-chromium alloys in a state of solid solutions (Nichrome) are good soldering alloys but possess a relatively high melting-point.

According to the equilibrium diagram of the Ni-B system, one of the eutectics of this system is formed at 1140°C . Boron has a reduced solubility in nickel and forms with it low-plastic alloys. The effect of beryllium on nickel alloys resembles in many respects the action of boron; beryllium has a reduced solubility in nickel and at a content of 5.2 % Be it forms a brittle eutectic which melts at 1155°C .

Manganese is one of the most important alloying constituents since it allows us to lower the melting point of nickel alloys without affecting their plasticity. Ni-Mn alloys have a low heat-resistance and are highly soluble in molten cadmium; by addition of 8-18 % Cr their heat resistance can be improved. Manganese is soluble in nickel in a quantity up to $\sim 43\%$. The lowest melting point of the Ni-Mn alloys is 1005°C (at a content of $\sim 60\%$ Mn and 40 % Ni).

At a zirconium content of $\sim 17\%$ Zr alloys form eutectics which

melt at 961°C. Due to the lower solubility of zirconium in nickel, any visible reduction of the melting point of these alloys without a simultaneous lowering of the plasticity seems to be unlikely.

Nickel-alloy systems and particularly the nickel-zinc alloys, forming peritectics with a reduced melting point, seem to have no larger possibilities.

Binary alloys of the Ni-Cu, Ni-Pd, Ni-Pt and the Ni-Au systems form a continuous series of solid solutions. The three latter systems form solid solutions with a minimum melting-point.

The endurance limit of Ni-Cu alloys is low; therefore, copper is not added to solders used in soldering heat-resistant alloys working at temperatures higher than 800°C. The influence of Pd, Au and Pt on nickel alloys has not received extensive investigation.

Nickel-base solders required for soldering of heat-resistant alloys should have a satisfactory heat resistance.

In the commercial heat-resistant nickel alloys, the basic hardening effect is due to aluminum and titanium forming both a high-dispersed phase on a Ni₃Al-base (in which a substantial amount of titanium may be dissolved). The solid solution of these alloys is hardened by elements like chromium, molybdenum, tungsten and cobalt.

Little has been published on the use and properties of nickel-base solders. Table 56 presents some compositions of nickel-alloys.

Solders with a high boron content (see Table 56) are brittle and are employed in powder form. These solders attack the base metal (e.g., on iron or nickel) since they easily form eutectics with it. Therefore, the duration of the soldering process and the size of soldering clearance should be as small as possible (the clearance should be within the limits of 0.025-0.05 mm).

Nickel manganese-rich soldering alloys are used in soldering heat-resistant alloys subjected to a temperature of 815°C. They are not attacked by liquid sodium and therefore may be used for soldering parts of sodium-cooled nuclear reactors.

Ni-20 % Cr and Ni-40 % Cr solders are solid solutions. Of the alloys which form continuous series of solid solutions (melting at 1237°C), the solder with 40 % Ni and 60 % Pd, has the lowest melting point and some plasticity and tenacity.

Solders containing 48-50 % Mo form a eutectic in the binary Ni-Mo system. Solders with an average content of 11 % P form a eutectic in the binary system Ni-P, and are composed of two phases: Ni + Ni₃P.

Table 56

Nickel-base solders

Composition of solder, %										Temperature, °C, of:			Remarks
Ni	Cr	Mn	B	C	Fe	Si	Other elements	Solidus	Liquidus	Soldering			
93.25	—	—	2.25	—	—	3.50	I	—	1050	—	193/		
91.25	—	—	3.25	—	—	4.5	I	—	1000	—	193/		
82.1	7	—	2.9	—	3	4.5	0.5	—	1000	—	193/		
71.25	16	—	3.75	—	4	4	I	—	1030	—	193/		
65—75	13—20	—	2.75—4.75	—	—	—	0.5	1010	1070	1100—1180	193/		
72.3	15.0	—	3.75	0.45	4.0	4.50	—	1010	1070	—	154/		
70.5	16.5	—	4.0	1.0	4.0	4.0	—	1010	1070	1150—1180	Colmonoy № 6194/		
60—85	up to 20	up to 30	0—3.0	—	B + Fe = 0—3%	0.5—2.0	Present	—	950—1070	950—1070	Nichrobraz 95/.		
40	—	—	—	—	—	—	60Pd	1237	1237	1285	196/		
71—81	10—17	—	2.0—4.0	—	—	—	$\Sigma(\text{Fe} + \text{Si} + \text{C}) = 9.0$	—	1060	—	198/		
90—83	8—14	—	2—3	—	—	—	$\Sigma(\text{Fe} + \text{Si} + \text{C}) = 8.0$	—	1100	—	198/		
80	20	—	—	—	—	—	—	1400	1420	—	189/		
60	40	—	—	—	—	—	—	1350	1365	—	189/		
40	—	60	—	—	—	—	—	1005	1005	—	189/		
32	—	68	—	—	—	—	—	1005	1010	1010—1070	198/		
50—52	—	—	—	—	—	—	48—50Mo	1300	1315	—	196/		
80	10	—	—	—	—	—	10P	880	900	1010	199/		
88—90	—	—	—	—	32—34	—	10—12P	1020	1030	—	196/		
58—54	—	54—57	—	—	—	—	10—12P	—	—	1120	196/		
36	7—10	—	—	—	—	—	—	—	—	—	Chromanil		
70	20	—	—	—	—	10	—	—	—	1175	196/		
											199/		

§ 14. Iron-Base Solders

According to the definition of the soldering process given by the AWS /54/, soldering alloys should not contain any iron; nevertheless, in practice instances are common when iron-base solders have been in use. For soldering of 30 KhGSA steel in a liquid salt bath, cast-iron solders having a low-melting point may be used /100/.

Table 57

Iron-base solders /98/

Composition of solders, %					Temperature of solidus, °C
Fe	Cr	W	Si	B	
90-83	7-11	—	2-4	1-2	1315
67-55	13-19	17-22	—	3-4	1260

For soldering high-speed-steel cutting edges or hard-alloy cutting edges to their holders, soldering powders of ferroalloys (ferromanganese and ferrosilicon) are required. These solders will be described later in Chapter V.

§ 15. Solders for Fluxless Soldering

Solders for fluxless soldering (the so-called self-fluxing solders), contain elements which accomplish the following fluxing functions: removal of oxides from the parts to be soldered; protection of the joints from oxidation during the soldering process; modification of properties on the surface of the molten solder in order to improve its wetting action on the base metal.

The solder for fluxless soldering operations should contain components that are liable to reduce the elements in the base metal from the oxides formed on its surface. The affinity of these soldering elements for oxygen should be higher than the affinity of oxygen for the metals from the oxides formed in the base-metal. Ordinarily, the chemical affinity is determined by the amount of heat release or the free energy of the reaction of oxidation. The so-formed new-oxides, unlike those obtained by a reduction process, should be easily removable from the surface of the soldered seam. This may be achieved in cases where the oxides themselves have a lower melting point than the soldering temperature or when they form low-melting compounds with the oxides of the base metals.

To such a group belong some alkaline metals as Na, K, Cs and Li. Addition of these elements to low-melting solders may assist in their action during soldering of carbon-steel and some nonferrous metals (alloys). They are rather undesirable in solders required for soldering alloys containing Ti, Al, Be, Mg, Cr etc, which create high-melting, chemically inert oxides on the surface of the base metal.

One of the alkaline metals, lithium, activates some silver solders used for soldering different steels, among them stainless steels. By addition of 0.5-1% Li to silver alloys with more than 50% Ag, these solders

become self-fluxing when soldering stainless steels in an argon atmosphere /101/ — /103/; due to this addition, soldering of steels may be performed in a hydrogen atmosphere with a dew-point 6-20°C higher than when soldering with the same solders but without addition of lithium /104/.

Self-fluxing solders of the Cu-P and Cu-Ag-P system are known for a long time, being used in cases where the flux can not be removed after soldering.

Fig.53 gives the equilibrium diagram for the alloys of the Ag-Cu-P /71/ system. At present, among this group of alloys, the self-fluxing solders with 7% P and some silver content are preferred since solders with 7% P content are very brittle. By adding a certain amount of phosphorus to copper and copper-silver solders they become self-fluxing as a result of the ability of phosphorus to reduce copper from its oxides and to form low-melting oxides which exert a fluxing action.

In Table 58 some grades of self-fluxing solders are listed.

Table 58

Composition and soldering temperature of some self-fluxing solders

Composition of solder, %									Soldering temperature °C	Grade of solder and its use
Ag	Cu	Zn	Sn	Cd	Ni	Mn	P	Li		
99.5	-	-	-	-	-	-	-	0.5	-	For soldering stainless steels in an argon or hydrogen atmosphere
78	21.5	-	-	-	-	-	-	0.5	-	
85	-	-	-	-	-	14.5	-	0.5	-	
72	27.5	-	-	-	-	-	-	0.5	880	
50	13-13.5	17	-	15	1	-	-	0.5-1	850	
50	14.4-14	17	-	15	-	-	-	0.5-1	850	-
71	28	-	-	-	-	-	1	-	800	For soldering copper and brass PSRMF-71-28-1-1
15	80	-	-	-	-	-	5	-	-	
5-10	90-83	-	-	-	-	-	5-7	-	-	
-	82	-	-	-	13	-	5	-	650	As a substitute for solders PSRMFN-28-1 & PFOTs7-3-2
-	90.5-86.5	1-3	2.5-3.5	-	-	-	6-7	-	730-750	

The PSRMF-71-21-2 solder has a good plasticity and is easily rolled into strips. The PFOTs7-3-2-solder is used for soldering of parts not subjected to vibrations or heavy impact loads. According to Bredzs /105/, by addition of 0.5 % Li and 1 % Ni to solders with 50 % Ag, 13-13.5 % Cu, 17 % Zn and 15 % Cd, they become self-fluxing not only in an argon atmosphere but also in air.

Addition of 0.12-0.25 % P to a solder containing 65 % Ag, 20 % Cu and

15 % Zn has also proved to be useful for soldering nickel austenitic stainless steel, monel metal, low-carbon-steel parts and copper-tungsten electrical contacts /101/. Addition of 0.12 P to this solder improves the wetting action of the solder on the base metal and greatly increases the strength of the butt-soldered joint. According to the authors' information, addition of phosphorus (1 %) to silver solders used for soldering stainless 1Kh18N9T steel in an argon medium has little effect.

When self-fluxing solders are used, heating of the parts to be soldered is to be done very quickly in order to prevent burning out of lithium or phosphorous from the soldering alloy and to avoid a strong oxidation of the surface of the metal to be soldered. The most suitable method of heating for this case is the electric-resistance and the gas-torch method. Furnace heating may not always yield good results. In soldering with self-fluxing solders, heating should be performed under a slight vacuum or in an inert medium (gas or hydrogen) to prevent oxidation of the base-metal.

High-silver solders (more than 50 % Ag) with a content of 0.5-1.0 % Li are used for fluxless soldering (in a pure argon atmosphere) of titanium and its alloys, and for soldering titanium to low-carbon and stainless steels, and to nickel and copper-alloys.

To the groups of self-fluxing solders may be attached also several boron-containing solders, particularly these of the Ni-Cr-Si-B system.

According to Setapen /106/, self-fluxing silver-copper solders with a content of 7.5 % Cu and 0.2 % Li are used for soldering nickel- and titanium alloys employed in honeycomb-type constructions as well as for soldering parts of rockets and guided missiles.

The eutectic Ag-Cu solder with 28 % Cu and 0.5 % Li, is used for soldering titanium-bearing low-carbon steels /107/.

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Chapter VI

FLUXES FOR SOLDERING OF METALS AND ALLOYS

Fluxes and non-metallic substances (with a non-metallic bond) are used in the process of soldering to protect the joint from chemical interaction with the environment, to clean the joined parts and the solder from impurities and products of chemical reaction with the environment, and finally to reduce the surface tension of the molten solder thus improving its spreadability.

The surrounding gaseous medium is liable to create oxides, nitrides, sulphurous compounds, and other non-metallic films on the surface of both the solder and the parts to be soldered. These non-metallic films, formed before and during soldering impede development of a metallic bond between the solder and the parts to be joined.

Soldering fluxes may be used in the solid, liquid or gaseous state but their effectiveness appears only when used in the liquid or gaseous state.

The fluxing substances should meet with the following requirements:

1. Except in cases of reaction soldering, chemical interaction between the solder and the flux should not take place; upon melting, the flux and solder should form two liquid immiscible layers. In many cases the chemical inertness of the flux and still more of the molten solder with respect to the base metal is a very relative one. So, for instance, alloying of certain metals in the liquid state is achieved by melting them under a layer of inorganic salts; improvement of the properties of silumin is achieved, e.g. through the modified foundry practice by adding sodium salts to the charge; manganese is added to the charge of magnesium alloys during the melting, together with fluxes containing manganese chlorides; in melting of many alloys, their saturation with boron is due to boron-containing fluxes used in the course of melting, etc.

Chemical interaction between flux and molten solder increases in intensity with the increase of the soldering temperature. In certain cases, the possibility to alloy solders in the process of soldering with metallic elements from the fluxes should not be overlooked. So, for instance, in soldering aluminum alloys with low-melting fluxes containing a large percentage of zinc or lithium chlorides or fluorides, zinc and lithium may be absorbed by the molten solder. Soldering of titanium alloys should not be performed with boron-containing fluxes in view of a probable alloying of the solder or even the base metal with boron etc.

The specific gravity of liquid fluxes should be, as far as possible, less than that of the molten solder.

2. The melting point of the flux should be lower than that of the solder. Before the solder starts to melt, the liquid flux should remove from the surface of the joined parts any impurities and non-metallic films and protect the parts from the action of the surrounding medium.

3. The flux should not interact chemically with the metals or alloys to be soldered, or at least its chemical activity should not exceed a minimum value. This refers particularly to the corrosive action of the flux on the solder and the base metal, which should be reduced to a minimum.

4. Fluxes should dissolve or destroy the non-metallic films formed on the surface of the solder and the parts to be soldered, as a result of the chemical action of the surrounding medium.

5. Liquid fluxes should exhibit good spreading and wetting ability on the solder and the soldered seam. The surface of the solder and the parts to be soldered close to the soldered seam, should be completely covered by liquid fluxes throughout the soldering process.

6. Both the molten and the gaseous flux should promote the spreading of the molten solder on the parts to be joined and strengthen its adherence to the base metal.

7. Fluxes should be stable during transportation, storing and soldering; possible changes in their composition should not affect the soldering process.

8. During heating for soldering purposes, the flux should not undergo marked changes in its chemical composition. Such changes may be caused by evaporation of the fluxing components, by chemical interaction between them and the solder or the base metal, by liquation phenomena during dip soldering, etc.

Certain fluxes are hygroscopic: absorption of moisture may change their activity during soldering. Therefore, they should be kept in airtight packings.

After soldering, any residues of flux should be removed from the surface of the soldered joint since certain active fluxes are liable to corrode the soldered joint.

Not all of the available fluxes meet with the above stated requirements. Certain fluxes exert only a protective action, i. e. in the course of soldering they should prevent chemical interaction between the surrounding medium and the base metal. Other fluxes applied in soldering may be termed active fluxes.

In some instances of soldering the fluxing substance is incorporated in the soldering alloy. The process involved is called reaction soldering: the fluxing solder interacts chemically with the base metal; alternately such a substance also may be termed reactive flux or reactive solder.

In selecting the proper flux the following conditions of soldering should be borne in mind:

1. During dip soldering, any form of water even that of crystallization, should be eliminated, since its presence may cause boiling and sometimes even blasting (explosions, when using containers for dip soldering).

2. In resistance soldering, fluxes should be in the state of electric conductivity (in aqueous or alcoholic solutions).

3. The degree of chemical activity of the flux determines the duration of the soldering process: in prolonged soldering a less active but stable flux is preferable whereas for rapid (fast) soldering, an active but not always stable flux may be better suited.

4. All other properties being the same, the less corrosive fluxes should be chosen for soldering purposes.

For the time being no comprehensive theory of fluxing is available. Certain hypotheses have been advanced to explain the action of different groups of fluxes. Groups of substances have been established, which may be used as fluxes in soldering definite joints of metals or alloys.

According to the degree of efficiency, fluxes may be classified as:

1. Protective fluxes; this group covers only one substance: colophonium and its alcoholic solutions.

2. Fluxes of the semi-protective type with a very low corrosivity, such as organic greases, mineral oils and stearin.

3. Fluxes with a relatively reduced corrosivity, such as several organic acids and their aqueous or alcoholic solutions and also chlorides and amine phosphides (aniline). In order to reduce the corrosivity of organic compounds they are mixed with protective or semi-protective fluxing substances.

4. Corrosive fluxes attacking instable oxides or acting at relatively low temperatures; in this group metallic chlorides should be included.

5. Corrosive fluxes acting on chemically stable oxides; orthophosphoric and hydrochloric acids are examples of such fluxes.

6. Corrosive fluxes attacking chemically very stable oxides; such fluxes are metallic fluorides, most frequently combined with chlorides or with boron-containing substances.

7. Corrosive fluxes acting at high temperatures; boron-containing compounds should be referred to this group. To explain the action of fluxes in soldering aluminium alloys, recently the theory of electrochemical destruction of the oxide films has been advanced /1/. Oxide-dissolving substances are not always suitable for fluxing purposes. So, for instance, carbonates and potassium sulphates, used in chemical analysis to convert oxides to soluble compounds, proved to be unsuitable for fluxing. Sulphuric and nitric acids, both strong solvents of oxides are also unsuitable as well as sulphates, nitrates and chlorates.

Many fluxes exert only a reduced dissolving action on metallic oxides. Consequently, the ability of a substance to dissolve oxide films is not a sufficient criterion for judging the suitability of a substance for fluxing purposes.

A straight chemical dissolution of oxides in fluxes apparently does not affect the removal of oxide films /2/.

Several fluxes interact chemically with oxides, converting them to other compounds which, single or combined with other constituents of the flux, become fluid at soldering temperature, e.g. some chlorides.

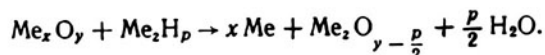
Certain fluxes form easily removable compounds with oxides, e.g. borates. The action of some fluxes on oxide films leads to formation of water and of compounds soluble in water, which float on the surface of the parts to be soldered.

Certain fluxes in interacting with oxides form volatile compounds and are able to clean the surface of the soldered seam (e.g. gaseous fluxes).

Several fluxes or products of their decomposition, in penetrating into the oxides, cause their mechanical destruction and promote floating up of the molten solder (the so-called reactive-fluxing solders).

A series of fluxes such as hydrogen and certain metallic hydrides

are effective in the course of the reducing reaction which may be written in the following form



Metallic hydrides may decompose to hydrogen which assures a protective atmosphere during soldering.

The function of a flux is not confined to removal of metallic oxides; the flux should also have protective properties and should be able to change the physical properties of the molten solder.

§ 1. Fluxes for Soldering with Low-melting and High-melting Soldering Alloys

According to Crow /3/, greases or mineral oils are able to dissolve oxides formed in soldering of sheet metals, but are unable to dissolve copper oxides. Industrial vaseline, sometimes used as a flux, interacts chemically with oxides because of its content in impurities of mineral acids.

At room temperature metaphosphoric acid is a solid, hygroscopic substance presenting some inconvenience for use as a fluxing agent. Orthophosphoric acid available in the liquid state is more suitable for that purpose. Solutions of orthophosphoric acid (with a concentration of 40-60 %) have been efficiently used in soldering aluminum bronze and stainless steels /4/, /5/. The FIM flux with a content of orthophosphoric acid has been used for soldering copper, brass and metals of the platinum group. These fluxes represent a mixture of 200 ml orthophosphoric acid (specific gravity, 1.7), 1 l ethyl alcohol and 1 l water. After soldering, the residues of the FIM flux must be removed by rinsing in alcohol.

In order to reduce the corrosive action of orthophosphoric acid on the parts to be soldered, various fluxes containing this acid have been suggested (e.g. organic aminophosphates, especially the anilinium phosphate $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_3\text{PO}_4$). Due to the decomposition of the flux during heating, an active part of the orthophosphoric acid is formed. Ethylene glycol or mineral oil is used as a solvent. One of these fluxes, used for soldering brass, stainless chromium-steel, zinc, cadmium or aluminum-bronze has the following composition: 34 ml anilin, 34 ml phosphoric acid, (specific gravity 1.75 g/cm^3) and 40 ml ethylene glycol /4/. This flux has a reduced electrical conductivity and may be used for soldering electric equipment.

After soldering, the residues of anilinium phosphate fluxes are only slightly soluble in water; thanks to their corrosion resistance, they need not be removed from the soldered joint.

Anilinium-phosphate fluxes are required in soldering tin, silver or cadmium-coated parts, and also in soldering copper, brass, silicon and phosphorus bronze, particularly in dip soldering.

Corrosive fluxes cannot be used in soldering certain conductive parts such as radio, telephone and other electrical equipment, since they may lead to destruction of the insulating material or at least to reduction of its resistance to moisture. This kind of equipment may be soldered with

colophonium fluxes since other fluxes may cause corrosion and reduce the properties of the conductive parts of electrical equipment. Colophonium used as a flux has the following characteristics: it is insoluble in water; it has no electrical conductivity; it does not corrode metals or alloys; it does not collect dust or dirt on the soldered joint*.

The main component of colophonium is abietic (silvic) acid ($C_{20}H_{30}O_2$) melting at $173^{\circ}C$. Molten colophonium is able to dissolve only a very thin film of copper oxide (orange-red color), i. e. it is a very feeble solvent of oxides. In a moderate climate, the colophonium layer left after soldering protects the soldered joint from corrosion.

Colophonium may be used in the form of a powder, of a solution in alcohol or glycerine, or it may be mixed with kerosene and gasoline (benzine). Such a mixture may have the following composition: 40 % colophonium, 50 % gasoline and 10 % kerosene. One of the main disadvantages of colophonium fluxes is their strong adherence to the metal; on the other hand, they may be easily removed by alcohol, gasoline, turpentine or alkalis. Addition of about 5 % stearin to a 25 percent solution of colophonium in alcohol improves the characteristics of the colophonium fluxes; they can be removed with a rag.

A mixture containing 10 % colophonium 20 % stearin and the remainder alcohol /6/, has also been suggested as a flux.

Colophonium fluxes are required for a soldering temperature up to $300^{\circ}C$ and are used for soldering silver and cadmium-coated parts, silver, cadmium, copper, brass and phosphorous bronze (particularly in dip soldering) with molten tin. At a soldering temperature above $300^{\circ}C$, colophonium is subjected to carbonization and may impede the soldering process. Soldering with colophonium fluxes at a temperature slightly above $300^{\circ}C$ may be done only through rapid heating, e. g. by high-frequency induction heating or by resistance heating.

Fluxes, the main component of which is aniline hydrochloride ($C_6H_5NH_3Cl$) have the same efficiency as anilinium-phosphate-fluxes. Hydrogen, evolved during heating of these fluxes, promotes removal of oxides from the surface of the soldered seam. These fluxes are used for the same purpose as anilinium-phosphate-fluxes /7/. Aniline-hydrochloride melts at $199^{\circ}C$, evaporates (boils) at $245^{\circ}C$ and is easily soluble in water or alcohol.

The practical preparation of similar fluxes is based on the following theoretical assumptions: organic phosphates and hydrate-chlorides are neutral substances; being heated during soldering, they decompose to a base and to an acid part which promotes removal of oxides. Upon cooling, the corroded acid-portion of the flux combines with the basic component thus forming again a neutral substance. Sometimes such substances are mixed with vaseline and colophonium and are then termed activated fluxes.

Among the fluxes of the organic-acid type, lactic acid has proved to be most efficient ($CH_3CHOH.COOH$). This acid may be used as an aqueous solution (15 % lactic acid, 84.8 % water and 0.2 % wetting agents) or mixed

* Sometimes colophonium may be used as a substitute protective-coating of parts subjected to galvanizing, if some portions of these parts are to be subsequently soldered for their ultimate assembling.

with colophonium (20 % by weight, colophonium, 5 % lactic acid and 75 % denatured ethyl alcohol) /7/. This flux has a reduced corrosivity and electrical conductivity; it is used for soldering electrical equipment. Lactic acid melts at 18°C.

Thanks to its exceptional properties, colophonium is used in some fluxes composed of inorganic or certain organic salts which efficiently act on oxides of copper, iron and their alloys. For that purpose, organic solvents, particularly alcohols are used. Table 59 lists some of these fluxes.

Corrosion of the soldered joint under the action of the residues of flux left after soldering may be reduced by adding to the fluxing substance, inhibitors, ordinarily required for retarding of corrosion in active corrodant-media. So, for instance, to the LK-lo flux the PB-5 inhibitor devised by S. A. Balezin a.o is added. This inhibiting agent consists of 77.32 parts by weight, of liquid aniline, 20.65 p. b. w. of urotropine powder, 0.2 p. b. w. copper sulphate, 0.37 parts sulphuric acid and 1.5 parts of distilled water.

Hydrochloric aniline is insoluble in colophonium, and after evaporation of alcohol it precipitates on the parts to be soldered causing a corroding action.

Some agents are added to improve the wetting power of the flux on the surface of the parts to be soldered. Such a wetting agent added in small quantities is sulpho-ricinic ammonium.

To the first of the fluxes listed in table 59, sometimes 4 % of salicylic acid is added to promote the process of soldering.

The following fluxes on a colophonium base, used in soldering water-tight tubing may be considered acidless fluxes; they consist of 50 g colophonium, 100 ml glycerine and 850 ml denatured alcohol. The noncorrosive VTS-flux required in soldering of copper, silver, platinum, and their alloys has the following composition: 100 parts by weight (p. b. w.) of vaseline, 10 parts salicylic acid, 10 parts triethanolamine and 40 parts ethyl alcohol; they are corrosion-resistant.

Similar fluxes should be used only if freshly prepared. To prevent evaporation of the flux, the parts to be soldered are to be rapidly heated in a gas flame which does not touch the fluxing substance.

Cadmium-coated brass, bronze or copper parts are properly soldered with fluxes on a colophonium-aniline or zinc-chloride base. In soldering cadmium-coated steel parts with colophonium-aniline fluxes, the steel parts should be subjected to a preliminary blanketing with a copper interlayer.

Hydrazine (N_2H_4) and its derivatives have also been suggested as a fluxing agent. These derivatives have a certain acidity and a strong reducing-capacity /13/. Such derivatives are: the hydrazine hydrochlorides $N_2H_4 \cdot HCl$; $N_2H_4 \cdot 2HCl$; $N_2H_4 \cdot H_3PO_4$, etc.

Fluxing substances are also 5-7 % aqueous or alcoholic solutions of hydrazine sulphate or phosphate or their mixture with zinc or tin chlorides. Hydrazine melts at +2°C and boils at +113.5°C /14/. Hydrazine and its salts are hygroscopic and explosive. Hydrazine-dihydrochloride ($N_2H_4 \cdot 2HCl$) melts at +198°C. Alcohol or water easily removes the remainder of hydrazine fluxes after soldering. One of the hydrazine fluxes has the following composition: 5-7 % hydrochloric hydrazine, 15-20 % glycerine and the remainder, distilled water /13/.

Certain fluxes containing hydrazine salts when used for soldering purposes do not attack aluminum or copper alloys /15/.

Table 59

Some colophonium-containing fluxes

Grade of flux	% of colophon.	Active substance		Solvent		Remarks (source of in-form.)
		Name of flux	Content %	Name of solvent	Content %	
-	96.75	Hydrochloric aniline	1.75	Glycerine or ethylene glycol	1.5	/8/
LTI-1	20-22	Hydrochloric aniline or tri-ethanolamine	6-8 2	Ethyl alcohol	70	/9/
LTI-115	24	Metaphenildia-mine, Tri-ethanolamine	4 2	idem	70	/9/
LTI-120	24	Hydrochloric di-ethylamine, Tri-ethanolamine	4 2	idem	70	/9/
-	20	Hydrochloric aniline	1	idem	79	/7/
-	35	Hydrochloric aniline, Tri-ethanolamine	3-4 2	idem	60	/10/
LK-2*	30	Zinc chloride ammonium, chloride	3 1	idem	66	-
-	20	Lactic acid	5	idem	75	/11/
-	44	Aniline, lactic acid	9 36	idem	11	/6/
-	5	Orthophosphoric acid	28	Methylic alcohol or ethylene glycol	67	/12/
KETs	24	Zinc chloride	1	Ethylic alcohol	75	-
KE	25	idem	-	idem	75	-
LK-10*	26	Ammonium chloride	3 1	Ethyl. alcoh. +10 % PB-5 inhibiting agent	60	-

* Devised by S.K. Lotsmanov and B.O. Katsman

M. Miller, the owner of American Patents No 2266060, 2291399, 2291400, 2291401, 2311599, 2383171 and 2383172, suggested the use of organic compounds that contain boron fluorides for fluxing purposes. According to M. Miller these fluxes are equivalent to the fluxing agents containing fluorides of alkaline or alkali-earth metals, but unlike the latter, after soldering they are insoluble in water, unhygroscopic and do not attack the soldered joints.

Commercially available active fluxes used in soldering of metals and alloys with low-melting solders have a limited amount of components (ZnCl_2 ; NH_4Cl ; HCl ; HF ; H_3PO_4) and solvents (water and alcohol) /see Table 60/.

Table 60

Fluxes for soldering with low-melting solders		
Fluxes	Oxides to be removed	Metals or alloys to be soldered
$\text{ZnCl}_2 + \text{NH}_4\text{Cl}$	Fe_2O_3 , Fe_3O_4 , FeO , NiO , Cu_2O , CuO , ZnO	Carbon and low-alloyed steels, zinc, copper, brass, bronze.
Weak solution HCl or ZnCl_2	Fe_2O_3 , Fe_3O_4 , FeO , NiO , Cu_2O , CuO , ZnO	Zinc, low-alloyed steel, copper, bronze, brass, nickel.
$\text{ZnCl}_2 + \text{HCl}$	Me_2O_3 , $\text{MeO} \cdot \text{Me}_2\text{O}_3$	Chromium steel, monel metal, nichrome.
$\text{ZnCl}_2 + \text{HF}$	Me_2O_3 , $\text{MeO} \cdot \text{Me}_2\text{O}_3$	Brass and bronzes containing aluminum, silicon and/or manganese.
$\text{H}_3\text{PO}_4 + \text{alcohol}$	Me_2O_3 , $\text{MeO} \cdot \text{Me}_2\text{O}_3$	Manganese-containing bronze; chromium steel

The aqueous solution of orthophosphoric acid (e.g. 40 % by volume) /12, 16/ is an efficient fluxing agent in soldering of chromium steels, where fluxes on a zinc chloride or ammonium base are unsuitable. Decomposition products of orthophosphoric acid cause after soldering, corrosion of the soldered joint. In order to reduce the corrosivity of orthophosphoric acid, a mixture of colophonium and orthophosphoric acid has been suggested, prepared in a common solvent, alcohol (since colophonium is insoluble in water).

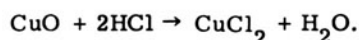
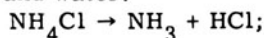
Aqueous solution of hydrochloric acid is an efficient flux in soldering stainless steel, monel metal and nickel-copper alloys.

Active volatile acid-fluxes (particularly hydrochloric acid) may be used for removal of oxide films in soldering of aluminum and its alloys. For this purpose, the solder is mixed with hydrochloric acid to form a paste which is then inserted into the gap between the parts to be soldered. Thanks to this procedure, formation of an explosive reaction can be avoided. Vapors of water and hydrogen chloride, evolved during soldering, destroy the oxide film and remove it from the surface of the soldered joint.

Of the soldering fluxes, most commonly used are the chloride salts. Some characteristics of chloride salts are given on the following pages.

Ammonium chloride has been used as a soldering flux since the sixteenth century. It has a white color, good solubility in water and lower solubility in ethyl alcohol. While heated in an ordinary atmosphere, ammonium chloride sublimates at 340°C. Only under high pressure, ammonium chloride can be liquified (at 500-600°C).

Solid ammonium-chloride is used to clean copper soldering-bits from deposits of cuprous oxides (Cu_2O and CuO). The reaction involved yields copper chloride, ammonia and water:



After heating ammonia dissociates to N_2 and 3H_2 , thus forming a protective medium.

Copper chloride form with ammonium-chloride soluble salts e.g. $\text{CuCl}_2 \cdot 6\text{NH}_4\text{Cl}$. The eutectic formed due to the combination of copper chloride with ammonium chloride melts at 140°C.

The fluxing action of ammonium chloride is based on the fact that this substance converts the metallic oxides to chlorides which together with ammonium chloride form low-melting, volatile or easily soluble eutectics or compounds. So, for instance, ammonium chloride forms with ferrous chloride (FeCl_3) a eutectic melting at 220°C (see Figure 55).

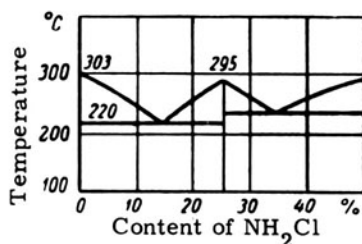
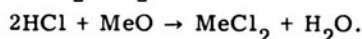
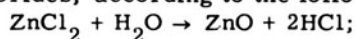


Figure 55. Equilibrium diagram of the FeCl_3 - NH_4Cl system

Zinc chloride has a white color; it is easily soluble in water or alcohol, and absorbs water vapors from the air, thus forming a liquid solution; its melting point is 283°C.

When used at high temperatures zinc chloride is able to dissolve certain metallic oxides; as a result of hydrolysis of the zinc-chloride solution, vapors of hydrogen chloride evolve which act on the metallic oxides, converting them to chlorides, according to the following reaction:



Metallic chlorides [MeCl_2] are more soluble than metallic oxides.

Vapors of hydrogen chlorides markedly increase the spreadability of tin-lead solders /18/, and reduce their surface tensions/11/.

The products of hydrolysis of zinc chloride are liable to intensify corrosion of soldered joints.

Based on the influence of hydrogen chloride on the spreadability of

tin-lead solders Dean and Wilson /18/ suggested several fluxes insoluble in water and resistant to any hydrolysis; while heated, these fluxes evolve hydrogen chloride but do not form products of reaction which would attack the surface of the soldered seam. Such fluxes are naphthalene tetrachloride, naphthalene tetrabromide, etc. On the other hand, according to the same authors, vapors of hydrogen chlorides exposed to the action of atmospheric moisture condense on the soldered seam, causing (to some extent) its corrosion.

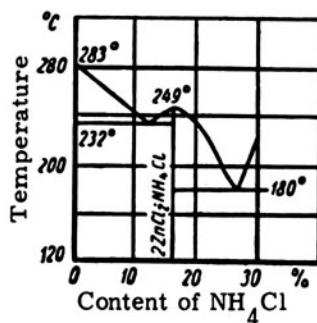


Figure 56. Equilibrium diagram of the ZnCl_2 — NH_4Cl system

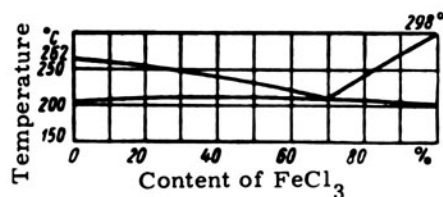


Figure 57. Equilibrium diagram of the ZnCl_2 — FeCl_3 system

Fluxing mixtures compounded of zinc chloride and ammonium chloride possess a greater activity than their individual component. The melting point of such mixtures is greater than that of zinc chloride. At a content of ~13% NH_4Cl , between ZnCl_2 and $2\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$ a eutectic is formed which melts at 232°C (Figure 56).

The compound $2\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$ melts at 249°C . At a content of 28% NH_4Cl , another more easily melting eutectic is formed which melts at 180°C . Mixtures of zinc and ammonium chlorides are unstable and upon heating may decompose to zinc-ammonium chlorides $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Zn}(\text{NH}_3)\text{Cl}_2$, which are also active fluxes. Ferrous chloride forms with zinc chloride a eutectic melting at 214°C (Figure 57).

The ZnCl_2 — NH_4Cl (28% NH_4Cl) eutectic or a mixture of about the same composition (55-75% ZnCl_2 and 35-25% NH_4Cl) as well as a mixture composed of 50% ZnCl_2 and 50% NH_4Cl have been suggested for fluxing

purposes. The latter may be used together with low-melting solders (92 % Pb and 8 % Sn; 98.5 % Pb and 1.5 % Ag; Zn, etc).

Proportions of zinc chloride and ammonium chloride most commonly used in fluxes are given in Table 61.

Table 61

Fluxes containing zinc and ammonium chlorides

Composition of flux, %					Application of flux for soldering of
ZnCl ₂	NH ₄ Cl	HCl (specific gravity 1.19)	H ₂ O	Vaseline	
48	-	-	52	-	Copper and copper alloys, carbon-steels
48	12	-	40	-	
40	20	-	40	-	
60	-	-	40	-	
48	-	10	42	-	Copper and its alloys
20	5	-	1	74	
48	-	22	36	-	Stainless steel
6*	4	5	85	-	Copper and ferrous alloys
10	-	35	55	-	
* Flux "Prima II"					

Fluxes, containing zinc or ammonium chlorides, should be kept in glass, ceramic or wood (packings) but not in metallic packings. These fluxes should not contain traces of copper, lead, or iron salts, since in soldering iron parts, these metallic compounds are chemically reduced forming a black tarnish on the surface of the parts to be soldered. The impurities of heavy metals in these fluxes may be removed by adding granulated zinc to them for several days. In a thoroughly cleaned flux, a fresh portion of granulated zinc should not be covered with black tarnish.

In order to improve the wetting power of certain fluxes on a metallic surface, an amount of 5-10 % glycerine is added. The "Prima I" flux used in soldering of copper, copper alloys and metals of the platinum group has the following composition: 73 g zinc chloride, 27 g ammonium chloride, 60 g glycerine, 1,000 ml methylic alcohol and 1,000 ml water.

The residues of fluxes containing chlorides of zinc, ammonium, cadmium or tin, promote corrosion of the soldered seam, and therefore, after soldering should be removed by rinsing in water or alcohol.

Some compositions of fluxes used in soldering with low-melting solders, may contain, apart from ZnCl₂ and NH₄Cl, fluorides, which are more active than chlorides, but many of them are poisonous. Such poisonous fluxes are, e.g. hydrofluoric acid formed in an aqueous solution of a flux which contains fluorides, fluoric-hydrogen formed upon decomposition of fluoride-containing fluxes and also potassium fluoride. Certain precautions should, therefore, be taken in using these fluxes.

Chloride fluxes are used in the form of solid mixtures, aqueous solutions, paste or viscous compounds. The paste or viscous form may be obtained by adding vaseline (e.g. 25 g ammonium chloride is mixed with 100 g vaseline at ~ 75°C), mineral oil, glycerine, spindle oil, wax, sizing and

other anhydride mixtures, e.g. 20 parts zinc chloride, 12 parts glycerine and 3 parts alcohol. Paste fluxes have the following composition: 1) 85 % vaseline and 15 % zinc chloride; 2) 65 % vaseline, 20 % zinc chloride, 3.5 % ammonium chloride and 11.5 % water; 3) 80 % vaseline, 16 % colophonium and 4 % zinc chloride; 4) 48 % spindle oil, 12 % bee wax, 15 % colophonium, 15 % glycerine and 10 % saturated aqueous solution of zinc chloride; 5) 70 % vaseline, 6.5 % paraffin, 23 % zinc chloride and 0.5 % ammonium chloride.

The following chlorides are used in soldering with low-melting solders: ZnCl_2 ; CdCl_2 ; PdCl_2 and AlCl_3 . Lead chloride is little soluble in water and has a reduced fluxing activity. Tin and cadmium chlorides are active but expensive fluxing substances. Cadmium chloride added to zinc chloride raises its melting point. For use in soldering with tinless low-melting solders, a mixture of glycerine with zinc and ammonium chlorides may be recommended [19]. Soldering copper and its alloys with zinc solders may be done with the FTs-37 flux which contain 5 % sodium fluoride, 37 % zinc chloride, 16 % lithium chloride, 31 % potassium chloride, 6 % sodium chloride and 5 % ammonium chloride added in a proportion to 3 cm³ water.

Soldering copper and copper alloys with cadmium-base solders at a temperature above 400°C may be done with the FK-30 flux which contains 50 % NaCl, 30 % CdCl, 15 % ZnCl and 15 % NH_4Cl .*

Chlorides and fluorides of various metals are also used as fluxes in soldering of aluminum and its alloys with aluminum-base solders. The main component of such fluxes is lithium chloride introduced first by Bates in 1900. Lithium chloride is very active and favors dissolution of aluminum oxides. Apart from this, lithium chloride added to mixtures of metallic chlorides, markedly lowers their melting point.

When the zinc-chloride content of fluxes used in soldering with aluminum solders exceeds 12 %, the pure zinc resulting from reduction of ZnCl_2 mixes with other components of the solder and develops on the surface of the soldered joint a deeper color than the solder.

Some fluxes prepared from metallic chlorides and fluorides are given in Table 62.

The KF- AlF_3 eutectic consists of 46 % KF and 54 % AlF_3 ; the flux No 17 composed of a mixture of fluorides, comprises 29 % LiCl, 59 % KF and 12 % NaF. The F370A flux and the flux No 17 may be used in various soldering processes e.g. in dip soldering and in soldering with molten fluxes. The F370A and F220A fluxes may be used in soldering of aluminum to copper and its alloys.

According to the electrochemical theory, the electrode processes on the boundary between the aluminum and the oxide film are of basic importance in the removal of the oxides films from the surface of aluminum [1]. The aluminum interlayer (support) serves as an anode, the oxide film being the cathode. Under the electrolytic action of the flux, the anodic portions of aluminum are dissolved, thus causing deformation and dividing of the oxide coating. The dispersed oxide-particles are then removed together with the fluxing substance. According to the same theory the processes of physical dissolution of the aluminum oxides have little influence on the removal of

* The fluxes FTs-37 and FK-30 have been devised by S. L. Lashko-Avakyan, K. O. Katsman and K. I. Soshnikova.

Table 62

Fluxes for light metals soldered with aluminium or magnesium-base solders /20-22/

Composition of flux % (by weight)													Grade of flux	Soldering temperature °C	Flux applied for soldering of
CdCl ₂	NaCl	KCl	LiCl	SrCl ₂	BaCl ₂	AgCl	ZnCl ₂	SnCl ₂	Mixture of fluorides	PbCl ₂	NH ₄ Cl	SbCl ₂			
-	35	35	20	5	-	-	-	-	-	-	-	-	-	-	Al
-	-	43.5	-	-	50	-	-	-	-	-	-	-	-	-	Mg
-	20	25	-	-	50	-	-	-	-	-	-	-	-	-	Al
-	38	-	-	-	55	-	-	-	-	-	-	-	-	-	Al
-	28	51	15	-	-	-	-	-	-	-	-	-	-	-	Al
-	5	48	37	-	-	-	-	-	-	-	-	-	-	610	Al
-	26	54	-	-	-	-	12	-	-	-	-	-	-	588	Al
-	16	32	32	-	-	-	12	-	-	-	-	-	-	593	Mg
-	5	48	37	-	-	-	-	-	-	-	-	-	-	538	Al
12	26	54	-	-	-	-	-	-	-	-	-	-	-	593	Mg
-	28	54	-	-	-	-	11.95	0.05	-	-	-	-	-	510	Al-Mn
-	30	36	18	-	-	-	7.9	-	-	0.1	-	-	-	588	Al + 2.5Mg + 0.25 Cr
15.95	24	52	-	-	-	-	-	0.05	-	-	-	-	-	593	Al-Mn
12.9	29	50	-	-	-	-	-	-	-	0.1	-	-	-	593	Al + 2.5Mg + 0.25 Cr
-	-	56	36	-	-	0.1	-	-	-	-	-	-	-	510	Al
-	-	57.7	36	-	-	-	-	-	-	-	-	-	-	510-590	Mg
-	-	50	32	-	-	-	12	-	-	-	-	-	34A	> 440	Al
-	-	47	38	-	-	-	10	-	-	-	-	-	F380	> 560	-
-	-	28	42	-	-	-	24	-	-	-	-	-	F320	> 350°	Al and its alloys
-	-	51	41	-	-	-	-	-	-	-	-	-	No.17	> 560	"
-10	-	47	38	-	-	-	-	-	-	-	-	-	F370A	> 560	"
-	-	-	-	-	-	-	90	-	-	-	8	-	F220A	> 220	"

the oxide film from the surface of aluminum. In computing the time required for a complete removal of oxide films from aluminum by fluxes containing a different amount of sodium fluoride, valuable data have been obtained (see Table 63).

Table 63

Composition of fluxes containing sodium chloride, and time required for complete removal of oxide film

Content of salts, in %					Time for removal of oxides from the surface of aluminum
KCl	NaCl	LiCl	Cryolite $3\text{NaF} \cdot \text{AlF}_3$	NaF	
38.6	34	17.4	10	-	2 minutes
42.75	37.75	19.5	-	-	35 % after 2 hours
42.65	37.75	19.5	-	0.1	70 % " 2 hours
42.25	37.25	19.5	-	1	80 % " 2 hours
41.75	36.75	19.5	-	2	1.5 hours
41.5	36.5	19	-	3	1.25 "
39.75	35.25	18	-	7	20 minutes
37.6	33.2	17.2	-	12	3 "

Aluminum test-specimens coated during heating with an oxide film, have been immersed in molten fluxes at 610-620°C. The time for the complete removal of the oxide film from the surface of aluminum is given in Table 63.

As shown, sodium fluorides and cryolite when added to metallic chlorides, foster the removal of oxides from the surface of aluminum. The action of fluorides is connected with a certain reduction of the dissolving potential of the aluminum anode.

Investigating corrosion of copper, bronze (7.5% Sn), brass (62.4 % Cu, 0.2 % Pb and the remainder, Zn), zinc and steel, covered with different fluxing agents (previously saturated with aqueous solutions of ammonium and zinc chlorides and also with a 10 % solution of lactic acid and a 40 % alcoholic solution of colophonium /23/), it was found that an aqueous solution of ammonium chloride constitutes the most corrosive medium. Throughout these investigations part of the test-specimens were permanently immersed and the other part periodically immersed in the fluxing substances. The above stated fluxes (except colophonium solution) are liable to corrode copper and bronze and to induce in brass intercrystalline corrosion phenomena.

Cryolite is of great importance as a flux in soldering aluminum parts since, in the liquid state, it is able to dissolve a certain quantity of Al_2O_3 . Cryolite is insoluble in water; at a content of 14.4 % Al_2O_3 it forms with the latter a simple eutectic structure at 950°C. In decomposing liquid cryolite forms two derivatives: NaF and AlF_3 which remain in a common solution.

Calcium fluorides also dissolve an appreciable amount of aluminum oxides (even in the solid state). Calcium fluoride (CaF_2) has found little

use for fluxing purposes. However, it is particularly efficient when added to fluxes with a high melting point since it increases their fluidity.

Certain cryolite-containing fluxes used in soldering on aluminum and its alloys are listed in Table 64.

Table 64

Cryolite-bearing fluxes for soldering of aluminum and its alloys

Composition of flux, %								Liquidus temperature, °C	Remarks
NaCl	KCl	LiCl	ZnCl ₂	BaCl ₂	SnCl ₂	KF	Na ₃ AlF ₆		
25	36	20	-	-	6	1	12	-	/20/
17	27	-	-	48	-	-	8	570	/24/
-	-	-	36	56	-	-	8	470	/24/
-	60	32	-	-	-	-	8	500	/24/
10	42.5	37	-	-	-	10(NaF)	0.5	380	/25/

Fluxes containing 36% ZnCl₂ belong to the group of reactive fluxes.

Sodium chloride forms with potassium chloride a continuous series of solid solutions with a minimum melting point of 658°C and at a content of 50% of components. Lithium and potassium chlorides form a simple eutectic which melts at 348°C and at a content of 42% molar KCl.

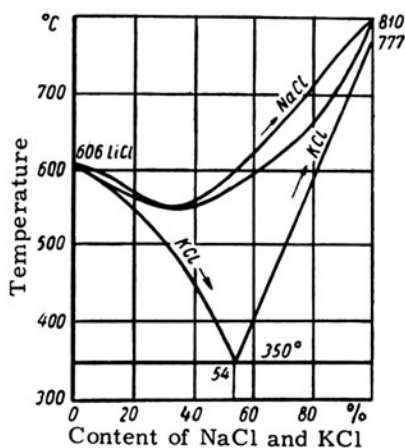


Figure 58. Recent fusibility diagrams of the LiCl-NaCl and LiCl-KCl systems.

The minimum liquidus temperature of this system is 553°C. The melting point of the above stated binary chloride system is given in Figure 58

/24/, /26/. The ternary diagram of fusibility for lithium, sodium and potassium chlorides is presented in Figure 59 /26/. The ternary eutectic containing (in molar proportions) 55% LiCl, 9% NaCl and 36% KCl melts at 346°C.

The exact equilibrium diagram for alloys of lithium chloride with calcium chloride is still to be established. The minimum temperature on the liquidus line of this system, according to some authors is 475°C at a molar proportion of 53% whereas other researchers indicate 480°C at a molar proportion of 39% CaCl₂.

The exact equilibrium diagram for potassium and calcium chlorides also is still unknown. In this system, KCl·CaCl₂ compounds and two eutectics melting at 600 and 640°C could be detected. Figure 60 presents the ternary diagram of fusibility for the LiCl-NaCl-CaCl₂ system (according to F. V. Kovalev and V. E. Plyushchev) /27/.

The following two eutectics given in molar proportions have been established: 1) 54.5% LiCl, 24.5% KCl and 31% CaCl₂ melting at 425°C; 2) 50.9% LiCl, 43.3% KCl and 5.8% CaCl₂ melting at 340°C.

Most chlorides and fluorides, except zinc and ammonium chlorides have a high melting point and therefore are unsuitable for soldering with solders having a relatively low melting point.

When mixed with chlorides, fluorides are more active than chlorides.

Basic components of the flux which assure a definite melting point, are chlorides to which ordinarily a relatively small amount of active fluorides is added, e. g. cryolite Na₃AlF₆ (in soldering of aluminum and its alloys).

Lithium chloride is added to reduce the melting point of fluxes; it is very hygroscopic and instable. Its relatively high chemical activity, as compared with other chlorides, may be attributed to its chemical instability and to the formation of active chloric hydrogen during heating of the aqueous solution of chloride. Lithium chloride forms with sodium chloride a continuous series of solid solutions with a minimum melting point of 550°C (at a content of 34% NaCl). With potassium chloride, lithium chloride forms a eutectic (at a content of 54% LiCl) which melts at 350°C (Figure 58). This eutectic is often used to obtain a flux with a low-melting point.

The ternary BaCl₂-KCl-NaCl system forms a eutectic which melts at 552°C (at a molar content of 42% KCl, 32% NaCl and 23% BaCl₂ or in parts by weight, 29% KCl, 19% NaCl and 52% BaCl₂) (Figure 61); the ternary system CaCl₂-KCl-NaCl forms a eutectic melting at 504°C (Figure 62). Thanks to their ability to form eutectics both systems are used as fluxes in soldering aluminum.

Barium chloride (35 %) forms with lithium chloride (65 %) a eutectic which melts at 510°C. Due to the great amount of lithium chloride involved, this eutectic is less suitable for fluxes with a low-melting point.

As a rule, certain metallic fluorides, particularly of the alkali group, are added in small quantities to activate fluxes of metallic chlorides. Initially, fluorides were used for soldering light metals, but subsequently they were also added to fluxes for heavy metals. The activating property of fluorides is connected with the evolution of a very poisonous gas, hydrogen fluoride.

Due to the toxicity of fluorides, great care must be taken in using them; this refers particularly to the water-soluble fluoride KF which melts at 857°C. NaF is less soluble in water, melts at 992°C, and has a lower toxicity than potassium chloride KF. Sodium fluorides form (at a molar content of 60% KF) a simple eutectic, melting at 710°C.

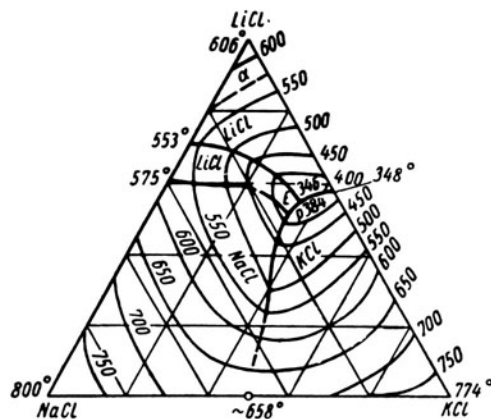


Figure 59. The surface of the liquidus area in the ternary LiCl-KCl-NaCl system

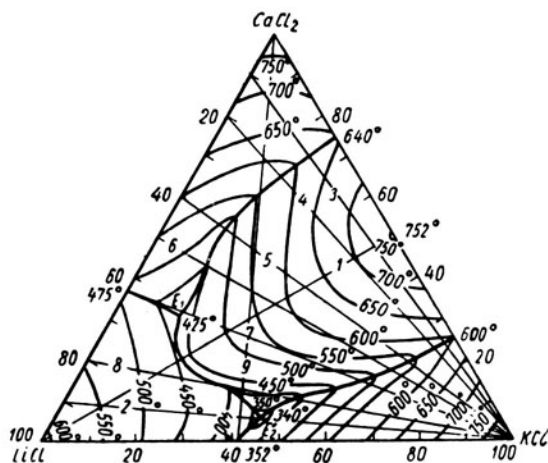


Figure 60. Equilibrium diagram of the LiCl-KCl-CaCl₂ system

Potassium fluoroborate KBF_4 is little soluble in water; while heated it decomposes to BF_3 which has an action similar to potassium fluoride. The melting point of potassium fluoroborate KBF_4 is 530°C . Calcium fluoride CaF_2 is insoluble in water and melts at 1330°C . The solubility of ZnF_2 in water is small; this fluoride melts at 872°C , and acts similarly to zinc chloride. Cadmium fluoride CdF_2 is little soluble in water and melts at 1100°C ; it is used as an active component in fluxes for soldering of aluminum and its alloys. Barium fluoride BaF_2 is insoluble in water and melts at 1280°C . Magnesium fluoride MgF_2 melts at 1270°C and is insoluble in water. In crystallizing, aluminum fluoride AlF_3 forms 3.5 molecules of water; on heating, the water of crystallization is evaporated; upon further heating, the aluminum fluoride evaporates (sublimates) at 1291°C without

being previously melted. This fluoride forms with other fluorides complex compounds, the most important of them being cryolite $\text{Na}_3\text{-AlF}_6$. Cryolite is insoluble in water and melts at 1000°C ; at a temperature of about 950°C it dissolves 15% Al_2O_3 forming with the latter a eutectic structure. Dissolution of aluminum oxides in cryolite occurs at a very high rate.

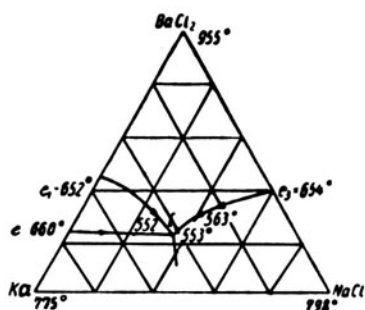


Figure 61. Equilibrium diagram of the ternary $\text{BaCl}_2\text{-NaCl-KCl}$ system (e_1 , e_2 , e_3 , E are eutectics of the system)

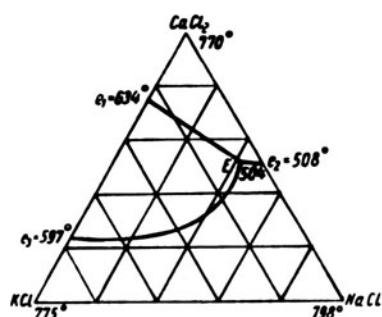


Figure 62. Equilibrium diagram of the ternary system $\text{CaCl}_2\text{-NaCl-KCl}$ (e_1 , e_2 , e_3 , E are eutectics of the system)

Cryolite, when added in a quantity of 8-10% to chloride fluxes increases not only their activity but also their spreadability [24].

In soldering many metals and alloys with solders melting at a temperature above 600°C , boric compounds (e. g. borax and boric acid) may be used as fluxes.

Boric acid H_3BO_3 occurs as hexagonal white crystals and may be dissolved in water, alcohol and mineral oils. Its specific gravity is 1.5 g/cm^3 . Upon heating to 100°C it loses water and forms HBO_2 ; upon further heating it loses the remainder of water and forms anhydrous boron trioxide B_2O_3 , which freezes to a vitreous substance. The melting point of this substance is 580°C . Anhydrous boron-trioxide evaporates at relatively low temperatures.

The main application of B_2O_3 for fluxing purposes is due to the fact that it forms with copper, zinc, nickel and iron oxides, relatively low-melting borates, metaborates, and other complex compounds (e. g. B_2O_3 , Fe_2O_3 , 4FeO).

Borates are little soluble in B_2O_3 ; therefore, in the presence of an excess amount of B_2O_3 , two liquid layers are formed, thus reducing the activity of such fluxes; B_2O_3 is used in soldering metals with relatively high-melting solders ($\geq 900^\circ C$) prepared on a copper base. Since zinc, chromium, silicon and aluminum oxides are little soluble in B_2O_3 , the latter is unsuitable for soldering alloys which form on their surface oxides of the mentioned type.

Borax ($Na_2B_4O_7 \cdot 10H_2O$) occurs as colorless transparent monoclinic crystals and is soluble in water; its specific gravity is 1.75 g/cm^3 . On heating, it loses water in the following proportion: at $100^\circ C$ it loses 5 molecules, at $130^\circ C$ 7 to 8 molecules; at $150^\circ C$ 9 molecules and finally at a temperature above $200^\circ C$ it loses the remainder of the water. Heating of borax is associated with violent boiling; therefore, prior to its use, it should be subjected to calcination. Borax melts at $743^\circ C$. In the liquid condition it decomposes to sodium metaborate and anhydrous boron trioxide according to the reaction:

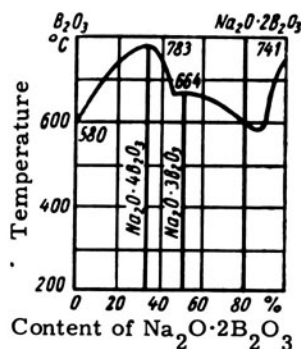


Figure 63. Diagram of the B_2O_3 — $Na_2O \cdot 2B_2O_3$ system.

When used as a flux, borax forms with the oxides relatively low-melting borates.

Borax is used in soldering with relatively low-melting solders (e. g. with silver solders).

The most commonly used fluxes are borax and boric acid. Their mixture leads to the following reaction: $Na_2B_4O_7 \cdot 10H_2O + 6H_2BO_3 \rightarrow Na_2B_{10}O_{16} \cdot 10H_2O + 9H_2O$.

Due to this reaction on the surface of the soldered joint, a layer of moisture is deposited.

With anhydrous boron, borax forms two compounds: $Na_2O \cdot 3B_2O_3$ and $Na_2O \cdot 4B_2O_3$. (see Figure 63).

Upon cooling of the soldered seam, the products of interaction between borax and the metallic oxides form a solid vitreous crust which firmly adheres to the surface so that its removal through mechanical cleaning presents some difficulties; it is little soluble in water.

The mixture of borax and boric acid is compounded in a definite proportion which depends on the melting point of the final flux.

$K_2B_4O_7$ and $Na_2B_4O_7$ form a continuous series of solid solutions with a minimum melting point of $660^{\circ}C$ and with a molar content of 35% $K_2B_4O_7$. The compounds KF and $K_2B_4O_7$ form a eutectic which melts at $680^{\circ}C$ (at a molar content of 80% $Na_2B_4O_7$). NaF and $K_2B_4O_7$ form a eutectic with a melting point of $712^{\circ}C$ at a molar content of 44% $K_2B_4O_7$ /28/.

Several mixtures of the derivatives $KF-NaF-B_2O_3$, used as fluxes, and containing the hygroscopic substances KF and B_2O_3 , are absolutely hygroscopic /29/.

In soldering brass, a flux containing 40% borax, 40% boric acid and 20% soda is sometimes used /30/. In order to improve the brass soldering process, sometimes chlorides are added to the mixture of borax and boric acid.

Two such fluxes have the following composition: 1) 58% borax, 40% boric acid and 2% calcium chloride; 2) 58% borax, 40% boric acid and 2% lithium chloride /31/.

Mixtures of anhydrous boron and borax have a weak fluxing action in soldering high-alloyed chromium steels and nichrome. For their activation, various salts are added. Active additives are fluorides of the alkali metals or fluoborates. Metallic fluorides are added to fluxes used at soldering temperatures of $850-1100^{\circ}C$; fluoborates are added in soldering at temperatures below $850^{\circ}C$.

The fluxing components are mixed in a prescribed proportion assuring the proper melting of the flux during soldering. Two such fluxes have the following composition: 1) 66% B_2O_3 , 19% $Na_2B_4O_7$ and 15% CaF_2 (anhydrous components the flux No. 200); 2) the flux No. 201, 77% B_2O_3 , 12% $Na_2B_4O_7$, 10%* and 1% of an intermediate alloy composed of 4% Mg , 48% Al and 48% Cu . According to some authorities, addition of this intermediate alloy may induce an aluminothermic reaction, but this is still to be proved. These fluxes are usually employed in a soldering range from 850 to $1100^{\circ}C$.

Sometimes they are used in a paste form. One such paste has the following composition: 45% H_3BO_3 , 10% $Na_2B_4O_7$ 35% KF and the remainder water.

Borates are only slightly soluble in liquid anhydrous boron; therefore when heating the mixture to elevated temperatures ($\sim 900^{\circ}C$), two liquid immiscible layers of borates and anhydrous boron are formed. Anhydrous boron, when used as a flux, despite its relatively reduced melting point, ($580^{\circ}C$) is efficient only at $900^{\circ}C$.

Since the metaborate $NaBO_2$ formed during heating assists in the dissolving process of oxides, borax when used as flux, is efficient at a temperature slightly higher than its melting point and below the temperature of the activity of anhydrous boron. Liquid borax dissolves a greater amount of zinc, cadmium, nickel, copper and iron oxides than molten anhydrous boron. Some information on the solubility of such oxides in boron compounds is given in Table 65 (referred to heating of 2g oxides in 20 g of flux at $760^{\circ}C$) /32/.

Due to an elevated melting point, anhydrous-boron, borax, and their mixtures are unsuitable for soldering various metals and alloys with silver solders having a melting range from 600 to $850^{\circ}C$. For that purpose, a mixture of anhydrous boron with fluorides, or a mixture of tetraborates with borax or anhydrous boron, is used.

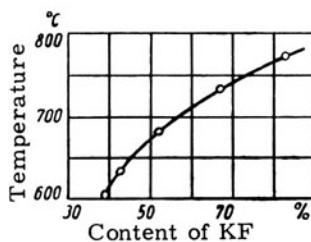
* [The name of material is missing in the Russian text.]

Table 65

Solubility of metallic oxides in borax and boric acid at 760°C

O x i d e	Weight of dissolved oxides, in g	
	In borax	In boric acid
Copper.....	2.0	0.56
Cadmium.....	2.0	0.86
Nickel	0.62	0.62
Copper.....	1.45	—
Iron	2.0	—

Until recently, a mixture of potassium fluoride with anhydrous boron has been used as a fluxing agent. Addition of potassium fluoride to B_2O_3 results in a continuous increase of the melting point which at a content of 50% KF attains the value of 675°C (Figure 64).

Figure 64. Variation of the melting point of the mixture B_2O_3 -KF.

The following is a typical composition of fluxes used in soldering turbine blades (particularly of Kh13 steel): 50% Kf and 50% B_2O_3 (43% KF + 57% H_2BO_3 ; 50% KF + 50% B_2O_3 ; 53% KF + 47% H_2BO_3 ; 60% H_3BO_4 + 40% KF) /33/, /34/.

Mixtures of anhydrous boron, borax, tetraborates or fluorides, proved to be more efficient fluxes. Due to the lack of an exact equilibrium diagram for these components, the choice of similar fluxes is so far limited. Data on certain binary systems with a content of fluoborates may be found in a study of Pinaevskaya and Chazova /35/.

At a temperature of 360°C and a content of 91% $NaBF_4$, potassium tetrafluoroborates form with sodium tetrafluoroborates a simple eutectic structure (Figure 65). The melting point of $NaBF_4$ is 370°C and of KBF_4 , 540°C. Potassium tetrafluoroborate forms with borax a eutectic of an unknown chemical composition (Figure 66). At a content of 80% $NaBF_4$, sodium tetrafluoroborate forms with borax an eutectic, melting at 270°C (Figure 67).

Soldering of structural and stainless steels, of copper and heat-resistant alloys requires fluxes containing (molten) borax, anhydrous boron and calcium fluoride. (Such fluxes are e.g. the flux No. 200 with $66 \pm 2\%$ B_2O_3 ,

$19 \pm 2\%$ $\text{Na}_2\text{B}_4\text{O}_7$ and $15 \pm 1\%$ CaF_2 ; the flux No. 201 with $77 \pm 1\%$ B_2O_3 , $12 \pm 1\%$ $\text{Na}_2\text{B}_4\text{O}_7$ and $10 \pm 1\%$ CaF_2 .) Potassium tetrafluoroborate at a content of 31% $\text{Na}_2\text{B}_4\text{O}_7$ forms with borax a eutectic, melting at 320°C (Figure 68). The binary equilibrium diagram of the system $\text{NaBF}_4\text{--K}_2\text{B}_4\text{O}_7$ is shown in Figure 69. The components of this system form a eutectic which melts at 270°C and contains 81% NaBF_4 . The components of the $\text{Na}_2\text{B}_4\text{O}_7\text{--K}_2\text{B}_4\text{O}_7$ system form a continuous series of solid solutions, with a melting point of 666°C and a content of 35% $\text{K}_2\text{B}_4\text{O}_7$ (Figure 70).

The ternary $\text{Na}_2\text{B}_4\text{O}_7\text{--KBF}_4\text{--NaBF}_4$ system has a eutectic which melts at 270°C and contains 19% $\text{Na}_2\text{B}_4\text{O}_7$, 19% KBO_4 and 62% NaBO_4 .

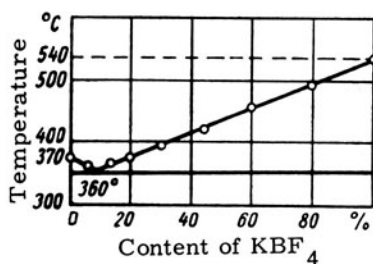


Figure 65. Equilibrium diagram of the $\text{NaBF}_4\text{--KBF}_4$ system

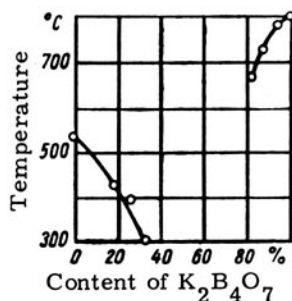


Figure 66. Equilibrium diagram of the $\text{K(BF}_4\text{)--K}_2\text{B}_4\text{O}_7$ system

Sodium and potassium tetrafluoroborates (KBF_4 and NaBF_4) have a good wetting action on the surface of metals and actively assist decomposition of metallic oxides. Potassium tetrafluoroborate renders metals more difficult to be dissociated than sodium tetrafluoroborate, and therefore, the latter should not be included in the composition of fluxes.

Potassium tetrafluoroborate has been suggested for fluxing as early as 1876 /36/, in soldering of cast iron, steel and brass. It may be used also in soldering silver and gold parts.

Several fluxes containing KBF_4 have been proposed for the soldering of chromium heat-resistant steels; such are mixtures of potassium fluoborate with borax or with sodium fluoride and anhydrous boron /37/.

Fluxes composed of anhydrous boron, borax, fluoborates and fluorides are still incompletely investigated. Only certain mixtures of these components have been used as fluxing substances.

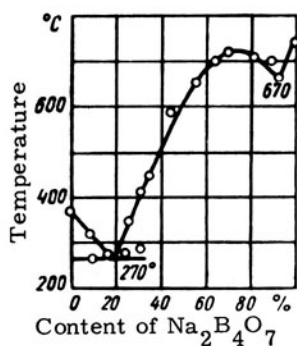


Figure 67. Equilibrium diagram of the $\text{Na}_2(\text{BF}_4)_2\text{-Na}_2\text{B}_4\text{O}_7$ system

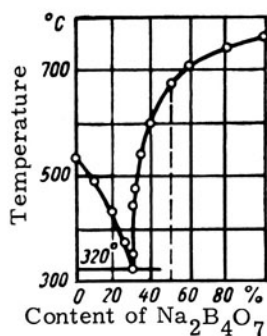


Figure 68. Equilibrium diagram of the $\text{K}_2(\text{BF}_4)_2\text{-Na}_2\text{B}_4\text{O}_7$ system

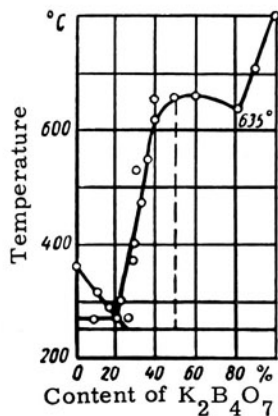


Figure 69. Equilibrium diagram of the $\text{Na}_2(\text{BF}_4)_2\text{-K}_2\text{B}_4\text{O}_7$ system

Certain fluxes suitable for soldering with silver solders are listed in Table 66.

The first two fluxes in this table are mixtures compounded of eutectics or close-to-eutectic alloys.

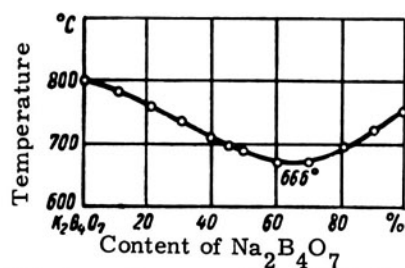


Figure 70. Equilibrium diagram of the $K_2B_4O_7$ - $Na_2B_4O_7$ system

Table 66

Fluxes containing potassium tetrafluoroborate

No.	Composition of flux, %					Remarks
	KBF_4	B_2O_3	H_3BO_3	NaB_4O_7	KF	
1	69-70	—	—	31-30	—	/34/
2	60	—	—	40	—	/33/
3	23 ± 2	35 ± 2	—	—	42 ± 2	No. 209
4	40 ± 2	25 ± 2	—	—	35 ± 2	No. 284
5	33.4	—	33.3	—	33.3	/36/
6	—	35	—	50	15	/33/

The third and fourth of these fluxes are mixtures of anhydrous boron and potassium fluoride to which an appreciable amount of potassium tetrafluoroborate has been added. The fourth of these fluxes has a lower fusibility than the third. These fluxes, when melted, do not form vitreous slags, and may be removed by boiling in hot water or in a 10% aqueous solution of citric acid.

The first two fluxes are unhygroscopic, the others are hygroscopic; they are suitable for soldering medium and high-alloyed steels (including stainless chromium-steels and also copper and its alloys) with silver-base solders.

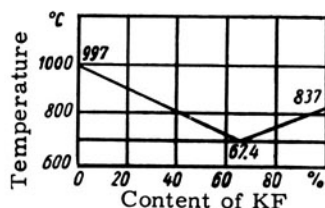


Figure 71. Equilibrium diagram of the NaF - KF system

Mixtures of potassium tetrafluoroborate are prepared by blending boric

acid with hydrofluoric acid (1 mol H_3BO_3 to 4 mols HF) with subsequent addition of a hot saturated KCl solution. As a result of the chemical reaction, the precipitate KBF_4 is formed. It should be taken into account that vapors of the fluxes No. 209 and 284 are poisonous, and therefore they should be used at $\leq 750^\circ C$ and under a fume hood since potassium tetrafluoroborate, when heated above this temperature decomposes, forms gaseous boron fluoride, BF_3 . The fourth and the fifth of the above listed fluxes adhere firmly to cold metals but not to hot parts. Besides, they have a great spreadability.

Sodium fluoride forms with potassium fluoride a simple eutectic at a 33% NaF content with a melting point of $700^\circ C$ (Figure 71). Similar fluxes may be prepared in a paste form by blending them with water, alcohol or tetrachloride of carbon.

Soldering high-melting metals with high-melting solders at working temperatures above $1250^\circ C$ requires fluxing substances with a higher melting point than that of the previously stated fluxes.

Largely applied are fluxing mixtures of anhydrous boron and various borates (particularly tetraborates $Me_2B_4O_7$, $R_2O \cdot 2B_2O_3$ and fluoborates $(BF_4)_nMe$). They have a high-fluxing power and a reduced corrosivity on alloys.

For the time being these mixtures are little investigated; this particularly refers to the equilibrium diagrams of mixtures composed of fluoborates /38/.

The following fluoborates may be used as fluxing components:

1) $(BF_4)Me^I$ or $BF_3 \cdot Me^IF$,

where $Me^I = Li, Na, K, Cs, Rb$ or NH_4 ;

2) $(BF_4)_2Me^{II}$ or $2BF_3 \cdot Me^{IIF}_2$;

where $Me^{II} = Cu, Ca, Ba, Mg, Zn, Co$ or Pb ;

3) $(BF_4)_3Al$ or BF_3AlF_3 .

§ 2. Gaseous Fluxes

Gaseous fluxes are used in furnace soldering and in the flame soldering process by means of a gas torch. In furnace soldering, fluxing is achieved by reducing gases (chiefly hydrogen) and by gases which constitute efficient components of liquid and solid fluxes (e.g. chlorine, fluorine, hydrogen chloride, hydrogen fluoride or boron trifluoride).

In soldering of steel parts, hydrogen chloride reacts with oxides and forms water vapors and liquid or gaseous compounds of chlorine with iron. However, hydrogen chloride also attacks the base metal.

Hydrogen fluoride has a reduced corrodant action on steel. In order to reduce the corrosivity of HF it is mixed with inert gases. During soldering, the reaction products of the flux (HF) evaporate, but in the gas-discharge collectors of the soldering unit, deposits of metallic fluorides are accumulated.

Ammonium fluoride is also used as a gaseous fluxing agent. Of the fluorine compounds, the most efficient proved to be ammonium fluoborate /36/.

Upon heating, ammonium fluoride decomposes to N_2 , H_2 , HF, and

ammonium fluoborate, to N_2 , H_2 , HF and BF_3 . Boron fluoride BF_3 has the best fluxing capacity and is less poisonous than hydrogen fluoride HF .

In gas-flame soldering, fluxing is accomplished by vapors of organic-boron compounds, particularly bormethylic or borethylic ether; these substances, when heated, decompose and form anhydrous boron which constitutes an active component of certain boron-bearing liquid fluxes. Anhydrous boron, when interacting with oxides, forms borates which remain on the surface of the parts to be joined.

When using organic boron compounds as fluxes, the process of hydrolysis involved should be eliminated or at least reduced to a minimum in order to avoid plugging of the flux-feeder*, and of the gas piping of the gas torch, by solid particles of boron acid.

For that purpose, hydrolizers of various constructions are used. At a definite proportion of methylborate to alcohol, the process of hydrolysis is retarded or even eliminated. One such flux has the following composition: 32% methylborate, 12% methylic alcohol and 56% acetone (see Asinovskaya in /39/). In soldering stainless steels, organic boron-containing compounds are inefficient; they should be mixed with volatile haloide compounds (see American Patent No. 2281910, 1942); such a flux should have the following composition: 28.2% methylborate, 10.6% methylic alcohol, 12% amyl chloride and 49.2% acetone. These fluxes are employed for soldering with silver solders.

To assure proper efficiency, similar fluxes should form azeotropic mixtures, i.e. mixtures which do not change in composition during partial evaporation.

Hydrolysis of such fluxes may be reduced or eliminated through:

1) changes in concentration of the solvent, thus displacing the hydrolysis reaction (acetone etc.); 2) adding to the flux special stabilizing agents (termed stabilizers) e.g. volatile silicon compounds /40/ etc.

§3. Removal of Flux After Soldering

Removal of flux after soldering is chiefly done by three methods:

1. By dissolution in water or in another liquid, subsequently rinsing in hot or cold water;

2. Through striking; mechanical shocks may be achieved by means of a hammer, a rubbing knife, a wire brush, through sandblasting or by means of a water or steam jet; thanks to the fragility of most of the fluxes involved, and due to their feeble bond with the base metal they may easily be removed by these procedures.

However, the probability of damaging the soldered joint by these procedures should not be overlooked; e.g. when the joint is struck in order to remove residues of flux, small particles of the latter may penetrate into the soldered joint.

* The flux-feeder of the FGF-1 type using the BM-1 flux has been devised at the VNII-Avtogen [Vsesoyuznyi nauchno-issledovatel'skii institut avtogen] (All-Union Scientific Research Institute for Autogenous Welding).

3. By sudden change in the temperature of the soldered joint; due to the different coefficient of thermal expansion of the flux and the base metal, to the brittleness of the flux, and also to the temperature gradient, the flux coating is destroyed and removed from the surface of the soldered joint. This procedure, termed also "thermal shock," is applied to remove the vitreous fluxes by immersing the still hot soldered parts in cold water. Nevertheless, it should not be applied when the soldered joint has a certain sensitivity to thermal shocks.

At present, remainders of flux are removed by certain physical methods, based on the different behavior of the base metal and the ionic compounds (fluxes) under different conditions. For instance, cavitation phenomena encountered in liquids and caused by ultrasonic oscillations are capable of intensifying destruction of the fluxing film.

Inorganic acids are soluble in water and hence easily removable. Chlorides of alkali and alkali-earth metals (e.g. zinc chlorides) used in soldering with low-melting alloys, are removed by hot water slightly acidulated with hydrochloric acid; addition of hydrochloric acid is required for dissolution of the products of interaction between the zinc chloride and the metallic oxides, which otherwise are insoluble in water. In order that the remainder of hydrochloric acid be neutralized, the soldered parts should be rinsed in hot water to which some crystals of caustic soda have been previously added, thus facilitating the final removal of the flux. When the soldered parts, prior to rinsing, have been exposed for some time to moisture in the open air, the water used for washing the flux should not be acidulated.

Zinc chloride may be dissolved in a solution of caustic soda (~10%) and then removed in running water. Remainders of flux containing metallic chlorides or fluorides after the soldering are removed with hair brushes, rinsing them for 8-10 minutes in water pre-heated to 50-80°C. The soldered parts are then rinsed for 30 min in running water and immersed for 5-10 min, in a 2% solution of chromic anhydride preheated to 60-80°C (for neutralization of the remainder of the flux and passivation of the surface of aluminum alloys); afterwards, the parts are rinsed again for 5 min in running water. The efficiency of removal of fluxing residues may be checked by means of a 2% solution of silver nitrate. Several drops of this solution are applied on the surface of the soldered joint; as a result, on places still covered with flux, white flakes of silver chloride precipitate are deposited. When this occurs rinsing is to be renewed. Residues of silver nitrate are removed by rinsing the joint in hot water. After final rinsing, the parts are dried at 120-160°C. If, after soldering, the joints are to be subjected to machining or mechanical cleaning (for removal of drops of solid solder or irregularities of the joined parts etc.), rinsing should be repeated since machining is liable to uncover pores containing residues of flux.

Anodic and phosphate coating of soldered joints for most solders and particularly for high-alloyed solders should be avoided since, in the course of preliminary pickling of the parts prior to their anode coating, they are covered with tarnish and are partially destroyed.

Varnish coatings applied on soldered joints protects them from corrosion.

Fluxes containing borax and anhydrous boron are removed by mechanical methods, e.g. by sandblasting or by rinsing in hot and then in cold running water followed by drying of the soldered joint. These fluxes may be

removed also by rinsing the soldered parts first in a 2-3% solution sodium or potassium bichromate heated to 70-90°C and then in a solution of the same substance but with a weaker concentration of the cold water solvent.

Fluxes may be removed from the soldered joint right after soldering but not later than an hour after completing the soldering operations.

Several organic acids used as fluxes are soluble in water and therefore, easily removable. Colophonium-containing fluxes are insoluble in water; in order to remove such fluxes, methylic and ethylic alcohols or trichlorethylene should be used. Reminders of colophonium on the soldered joint need not be removed since they do not corrode the metallic joint.

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Section Four

METHODS OF SOLDERING METALS AND ALLOYS

Soldering may be defined as a process of assuring a permanent joint by means of soldering alloys (solders). This involves proper design of the parts to be soldered. Design in soldering technology includes the following steps: 1) selection of proper methods of heating the parts to the soldering temperature and to the temperature of cooling after soldering; 2) selection of the proper clearance between the parts to be soldered; 3) selection of conditions for removing from the surface of the soldered joint and the solder, any film of foreign matter which does not firmly adhere to that surface (most frequently oxide films); 4) selection of proper methods for inserting the solder between the parts to be soldered, thus insuring after melting of the solder, a rigid metallic bond between the parts.

The above considerations are fundamental for the selection of a proper technology for soldered joints.

Soldering processes in which soldering is achieved mainly by the action of capillary forces (soldering proper) are in extensive use, whereas processes in which soldering is accomplished by gravity (brazing or bronze welding) are less developed.

Figure 72 shows a diagrammatical representation of various soldering methods applied at present. These methods are classified according to the method of heat transfer from the heat source to the parts to be soldered, and also according to the methods of creating the heat source in the parts involved.

Two basic methods of heating the parts to be soldered are applied: heat conduction and electrical methods.

At present not all of the existing heat conduction methods are applied; this particularly refers to the heat generated by the aluminothermic and some other exothermic reactions.

The diagram does not include the methods of forge heating (respectively furnace heating) and of indirect heating by preheated solid bodies (heated bricks, metallic blocks, etc) since they are little used at present.

Figure 73 gives a diagrammatic representation of soldering methods classified according to the methods of removal of foreign films formed before and during soldering on the solder and joint surfaces. In this diagram, this film is arbitrarily referred to as "oxide film", but in dependence on the gaseous medium involved, it may be a nitride, sulfide film, etc.

Most commonly used are the methods of filling the gap between the parts to be joined with finished solders available in various shapes. Soldering methods in which the solder is formed during the main soldering process as a result of a chemical reaction, refer to the reaction soldering process and are only seldom applied.

At present, two kinds of reaction-soldering processes are used:

1) the contact reaction-soldering in which liquid solder forms as a result of heating of solid metals or alloys while in contact; 2) reducing reaction-soldering in which liquid solder forms due to the chemical reduction of the

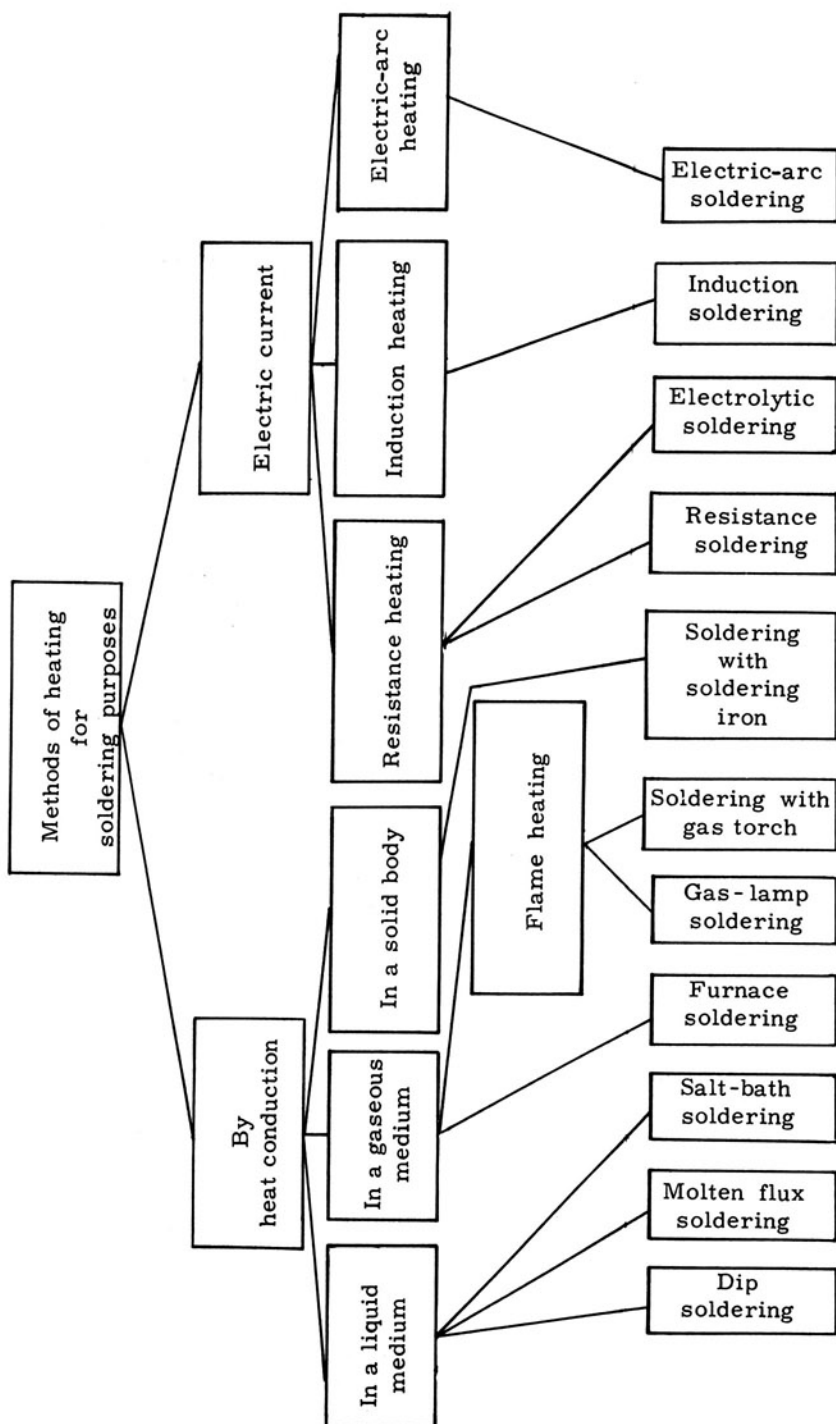


Figure 72. Diagrammatic representation of soldering methods, according to the methods of heating

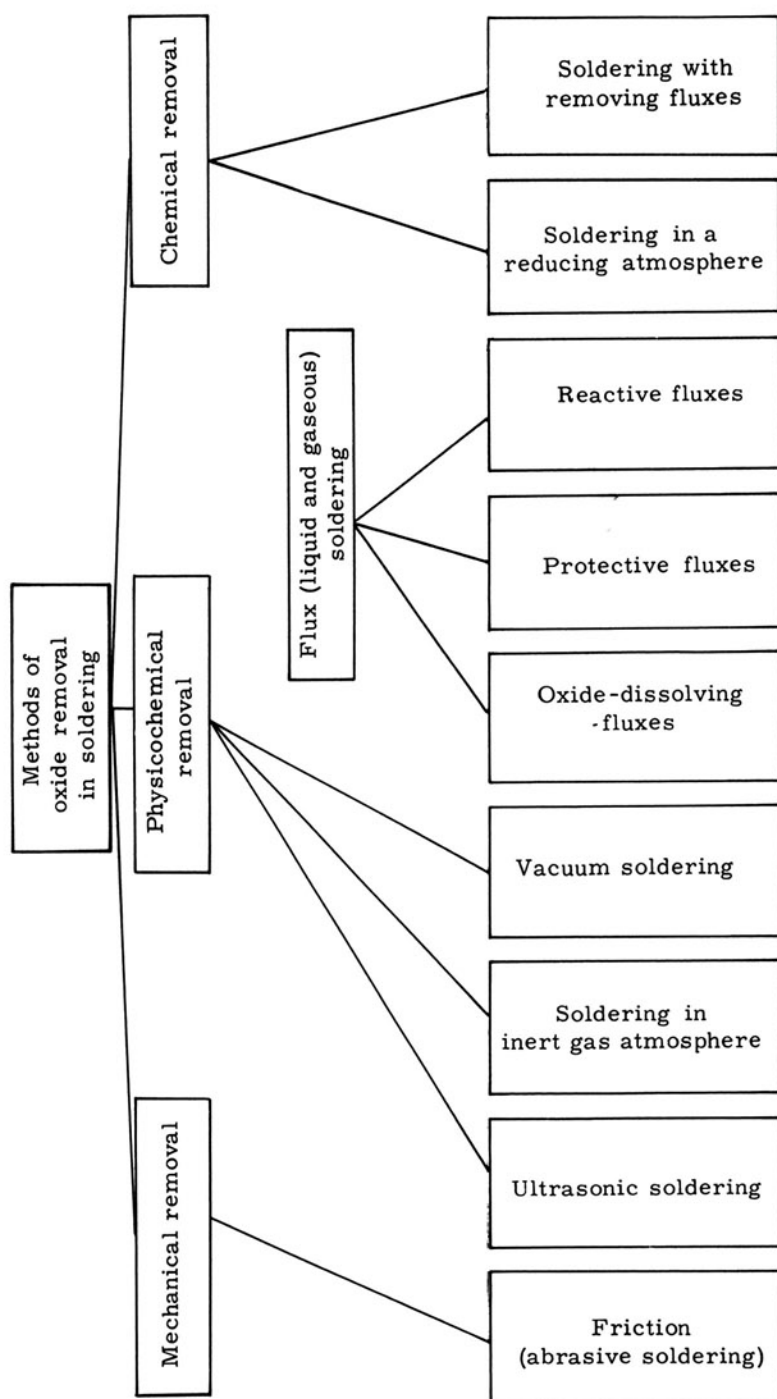


Figure 73. Diagrammatic representation of soldering methods, classified according to the method of oxide removal

fluxing substance involved. Methods of obtaining liquid solder as a result of the reaction with a substance other than a flux, are chiefly employed in soldering metals to a ceramic base (by reduction from oxides or by evaporation of the hydrogen from certain metallic hydrides). These methods are discussed later in this text when considering soldering of metals on ceramics.

Chapter VII

PREPARATION AND TINNING OF THE PARTS PRIOR TO THE SOLDERING OPERATION

A rigid bond between the solder and the parts to be soldered can be obtained only when the contact between them has sufficient rigidity. Usually, the surface of metals and alloys to be joined is covered with a layer of oxides, grease, dust, dirt, paint, etc., which impede an intimate contact between the base metal and the solder. The ability of a molten solder to flow on a prepared surface depends to a large extent on the condition and aspect of the surface. Therefore, prior to soldering, the surface should be properly prepared; this is done by: 1) removal of scale (including the oxide film); 2) proper cleaning of the surface of the future seam; 3) removal of grease, oil, dirt, dust, paint, etc.

§ 1. Removal of Grease, Oil or Dirt from the Surface of the Parts

Removal of grease, oil or dirt from the surface of the parts to be soldered may be done by various methods: by rubbing and rinsing the metal-surface in organic solvents and by rinsing in special ultrasonic baths.

For rinsing, the following organic solvents are used: ethylic alcohol, tetrachloride of carbon, refined (aviation) gasoline, trichloroethylene and perchloroethylene.

Degreasing baths for various metals and alloys consist mainly of an aqueous solution of alkalies or alkaline salts.

In the following, composition of such baths and the working conditions for iron, copper, nickel, and their alloys, is given:

- 1) 10 % solution of NaOH and the remainder, water; temperature of bath, 80-90° C; duration of immersing, 8-10 min.
- 2) 10 % solution of soda (Na_2CO_3) and the remainder, water; temperature of bath during degreasing, 100°C;
- 3) 10-20 g/l caustic soda, 25-50 g/l calcinated soda or trisodium-phosphate and 3-5 g/l water glass; bath temperature 80-90° C; duration of immersing, 10-45 min.

Degreasing of aluminum and its alloys may be accomplished in a bath of the following composition: 40-60 g/l commercial (industrial) trisodium-phosphate $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$; 8-12 g/l caustic soda (NaOH) and 25-35 g/l

water glass. The bath temperature during degreasing is 60-70° C; duration of degreasing is 3-5 min.

Sometimes degreasing of hard-alloy plates and steel parts may be done by boiling them in a borax solution.

Preserving grease applied on magnesium and magnesium alloyed parts may be removed by immersion in a 0.5-1 % aqueous solution of soda, heated to 100° C for 20-30 min, followed by rinsing in warm water and drying at 60-80° C.

Degreasing and cleaning of a large quantity of small irregularly shaped parts may be done also in special ultrasonic baths /1/. The ultrasonic set-up consists of a high-frequency oscillator (vibrator) of the magnetostriction or piezoelectric type, and of a bath with a rinsing fluid. Magnetostriction oscillators are economically more advantageous.

Ultrasonic cleansing may be applied to parts of various metals or alloys and is accomplished in the following manner. The parts to be cleaned are immersed in gasoline or a mixture of gasoline and acetone (1:1)* which serves as a bath for ultrasonic cleaning. High-frequency oscillators of various sizes and shapes induce in the bath oscillations of ultrasonic frequency (up to 40 kc/s). Cleaning is achieved quickly (max. 50 sec) provided the parts are 12.7-15.2 cm from the oscillator, and only in places where the parts touch the bath. Parts with deep holes should be shaken while immersed, in order to remove air from the holes. Thick-walled parts should be cleaned by means of double-sided oscillators. The cleanliness of the parts, obtained by ultrasonic treatment is higher than by usual rinsing in solutions.

Efficiency of ultrasonic degreasing and cleaning increases with the increase in density of the fluid bath and with the reduction of its volatility.

For removal of thick layers of grease (e.g. lubricating grease) the requisite duration of treatment in an ultrasonic bath is 1-3 min. After rinsing, the parts are dried in open air or blasted with a jet of compressed air.

The ultrasonic method is efficient in removing scale and rust. Rusty steel parts are cleaned by immersing in an ultrasonic bath composed of a 20 % solution of sulphuric acid (H_2SO_4) to which abrasive powder (boron carborundum, grain size No 70) in a proportion of 120 g to 1 l of solution has been added. Scale may be removed by immersing for 20-25 min in a solution of ammonium carbonate (of various concentration) to which the same abrasive powder has been added.

The previously stated results have been obtained by means of an oscillator with an output power of 500 w and a power consumption of 1,500 w, working in a wave band of ultrasonic oscillations (18-36 kc/s).

Ordinarily, ultrasonic cleaning is applied after preliminary removal of large particles of dirt by means of a water jet. The fluid of the ultrasonic bath should be periodically filtrated, in order to eliminate any foreign matter.

Degreasing of metallic surfaces may be also done by special vacuum cleaners /2/.

* According to data by I. V. Fomicheva and N. S. Tsukanova.

§ 2. Methods for Mechanical Removal of Scale and Oxide Films

In view of subsequent soldering, sometimes the parts prepared are covered with a thick layer of scale formed during previous heat treatment or hot working. This scale layer may be removed mechanically.

Thick layers of scale, rust, old paint, etc deposited on steel or iron parts, may be removed by means of a pneumatic hammer, the working tool of which consists of several bits fixed to a piston operated by compressed air. The compressed air removes at the same time pieces of loose scale left on the surface of the parts. /3/. Thick layers of scale on steel and iron parts may be removed also by quick and intense heating of the scale while the metal is cold. Due to the different coefficients of thermal expansion of the base metal and the scale, the scale cracks and may then be removed from the surface of the metal /4/.

Surface cleaning by sandblasting or shot blasting is used prior to soldering in the preparation of parts with a large and irregularly shaped surface. This method is chiefly applied for cleaning of iron and its alloys; aluminum, magnesium, tin and zinc alloys are not cleaned by this method.

As shown by experience, after sandblasting, the surface of the parts is poorly wetted by solders and often not wetted by fluxes, due to residues of sand particles left on the surface after sandblasting. Therefore, such a sandblasted surface should be subjected to additional cleaning of sand particles. Usually, this is done by polishing, by abrasive grinding and filing, and by pickling.

Shotblasting of metallic surfaces is more suitable when preparing the parts for soldering; sometimes this method is applied even for a final removal of oxides /5/.

In steelbrushing the parts after soldering, the pile of brushes used for cleaning carbon-steels, copper of titanium, should be relatively short and of sufficient rigidity. Cleaning of zinc, tin, and nickel-parts should be done with brushes having a fiber pile.

Size and direction of microirregularities on the surface of the parts to be soldered do not affect the rigidity of the joint, but have a definite influence on the spreadability of the molten solder. This influence is more intense the lesser the solubility of the base metal in the molten solder. Solders, weakly dissolving the base metal, have a much poorer spreadability on a polished surface than on rough one previously prepared by cleaning with emery cloth, metallic brushes or shavers. This refers to instances of soldering steel with copper and silver solders, and of soldering copper and steel with tin solders.

The influence of roughness apparently may be explained in this case by the fact that scratches act as capillary channels assisting the spreading of molten solder.

Roughness is a very important factor when the molten solder (e.g., in soldering of aluminum and its alloys with aluminum-base solders) quickly dissolves the base metal.

Surface roughness expressed in microns, is measured by means of special devices such as feeler-profilometers (Kiselev and Abbot profilometer) or optical-mechanical profilometers (Levin and Ammon profilographs) /7/ - /9/.

Some data about roughness measurements on metallic surfaces obtained by means of certain methods of mechanical working, are given in Table 67.

In order to ensure a thorough wetting action of molten solders on the base metal, its surface roughness should not be smaller than 10-15 microns; in assembling parts with a press fit, the surface roughness should be 80-150 microns, which may be attained by knurling. /5/.

Mechanical cleaning of surfaces is chiefly used for steel, copper, nickel and their alloys; for aluminum, magnesium, titanium and their alloys, pickling is a more adequate method for removal of oxide films.

Table 67

Roughness of metallic surface resulting from various methods of machining

Type of machining	Measured height of irregularities (roughness), in microns	Feed in mm	Length of investigated portion, in mm
Polishing	0.05-0.15	-	
Finishing, lapping, etc.	up to 1.0	-	0.15
Finishing; diamond finishing, finish-grinding	0.15-4.0	-	2.0
Semi-finish turning, milling, grinding, shaving	0.1-25.0	-	-
Planing or turning	0.8	0.05	-
	1.57	0.12	
	3.12	0.25	
	6.25	0.50	
	12.5	0.75	
Face milling or end milling	1.57	0.25	-
	3.12	0.50	
	6.25	2.5	
	12.5	2.5	
Milling with circular milling-cutter	1.57	1.25	-
	3.12	1.87	
	6.25	3.12	
	12.5	6.2	
Roughing	250.0	-	3-4

After cleaning with emery cloth, residues of emery cloth, left on the surface of the soldered parts, are to be wiped with a rag wetted with gasoline or another solvent.

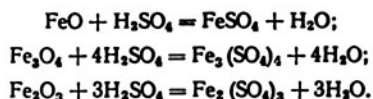
§ 3. Chemical Methods for Descaling and for Removal of Oxide Films

Cleaning of metallic surfaces by pickling, is based on the ability of various acids and alkaline substances to dissolve oxides of certain metals. Pickling is done by means of aqueous solutions of sulphuric, nitric, hydrochloric or anhydrous hydrofluoric acids or their mixtures, by aqueous solutions of caustic soda and also by gaseous pickling agents.

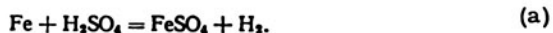
After pickling, the microrelief of the surface is better fitted for soldering than a mechanically cleaned surface.

In mass production, pickling is more efficient than mechanical cleaning of the surface. Among the disadvantages, overpickling of the surface and difficulties in handling the pickling agents should be mentioned.

Removal of oxides from iron and low-alloy steels by pickling. In order to remove oxides from the surface of iron and low-alloy steel parts, aqueous solutions of sulphuric and hydrochloric acids are employed. Removal of ferrous oxides FeO , Fe_2O_3 and Fe_3O_4 is achieved in solutions of sulfuric acid according to the reaction:



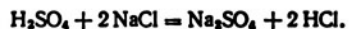
Iron sulfates formed during the reaction are mechanically removed together with remainders of scale by the hydrogen bubbles evolved in the course of the reaction between iron and acid:



Hydrogen, evolved between the scale layer and the base metal, causes cracking and destroying of the oxide film. During pickling in a solution of sulfuric acid, the mechanical action of hydrogen on the oxide film prevails over the action of chemical solvents on oxides /10/. In case of an intense reaction, the dissolution of iron in sulfuric acid / according to reaction (a) / is liable to cause overpickling and hydrogen-saturation of the metallic surface; to avoid this, pickling is to be performed very quickly.

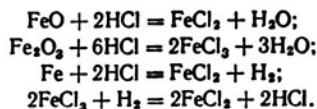
To prevent overpickling and hydrogen-saturation of iron and steel surfaces when pickling in sulfuric acid, small amounts of inhibitors are added to the pickling bath (0.2 % of the weight of the bath), which slow down the course of the reaction (a) and the rate of diffusion of hydrogen into steel, and favor dissolution of the oxides. Various inhibitors have been suggested, for instance, sodium oxide /11/, and the known inhibitors GM and PB /12/. At a definite content of H_2SO_4 and HCl in the pickling solution, uniform dissolution of the superficial oxides can be obtained. After pickling in sulfuric acids, steel parts are to be dehydrogenated in a thermal cupboard by heating to 180-200°C without overpickling the base metal. Most efficient is a mixture of 1 part HCl , and 3.5 parts H_2SO_4 .

Hydrochloric acid may be replaced by table salt (NaCl). The reaction of table salt with sulfuric acid yields hydrochloric acid:



The mixture is prepared by adding to 1 l of an 8-10 % aqueous solution of sulfuric acid, 30 g table salt.

The action of hydrochloric acid on the metallic surface covered with a film of iron oxides, occurs according to the following reaction:



As it can be seen, interaction between hydrochloric acid and iron or steel parts, does not lead to any evolution of hydrogen /13/.

Metallurgical practice employs special pickling solutions for pickling of steel parts prior to their soldering; after pickling, the parts are rinsed, neutralized in alkaline baths, rinsed again and then dried.

Such baths contain 5-10 % H_2SO_4 and 2-10 % HCl with small additions of KS or ChM additives ~0,2 % of the weight of the bath.

Pickling is carried out for 2-10 min at a temperature of 20° C /10/, /14/, /15/.

In certain cases, the method of gaseous pickling is used, in which the surface oxides are removed from steel or iron parts, by attacking with hydrogen-chloride gas at elevated temperatures (540-735° C).

Gaseous pickling is carried out in hermetic, externally heated, chromium-nickel steel chambers, or in internally heated refractory-lined chambers.

The mixture of 20 % HCl, 10 % CO_2 and 70 % N_2 , generally used for this purpose is obtained by blending, in definite proportions, combustion products of methane with dehydrated combustion products of natural gases, burnt in open air in the presence of chlorine.

Gaseous pickling involves no preliminary degreasing, since grease is burnt in the preheating furnace (at 600-730° C). In gaseous pickling the metallic surface is not saturated with hydrogen; duration of pickling is 50-60 sec. The reaction products of gaseous pickling are anhydrous salts. Being poisonous, pickling gases should not penetrate into the shop's atmosphere. /16/.

Removal of oxides from stainless steel by pickling. Oxides on the surface of stainless steel parts cannot be removed in pickling baths composed of aqueous solutions of H_2SO_4 and applied to low-alloyed steels. Oxides formed on the surface of stainless chromium steels, dissolve in aqueous solutions of mixtures of various acids, such as H_2SO_4 , HCl, HF and HNO_3 (Table 68).

Prolonged pickling in the bath No 5 (see Table 68) is not advisable since it may cause deep spot corrosion. To ensure a deeper pickling action and to obtain a rough surface, after pickling in the bath No 5, the parts are to be immersed in a 25-30 % solution of HCl. Pickling with this solution should be done until the surface of the metal is covered with a black tarnish /19/.

Deep pickling of tungsten molybdenum-bearing stainless steels is achieved in a 10 % aqueous solution of aqua regia: 3 % HNO_3 , 7 % HCl and 90 % water (parts by volume) at 80° C /20/.

After pickling, the stainless steel parts are to be thoroughly rinsed and brushed in hot water, in a 10 % solution of soda and again in water.

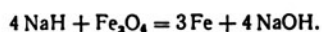
Table 68

Pickling baths (aqueous solutions) for
stainless steels /15/, /17/, /18/

No of bath	Composition of bath,% (parts by volume)							Temperature of pickling, °C	Applications
	H ₂ SO ₄	HCl	NaCl	HNO ₂	HF	CuCl ₂	NaNO ₂		
1	7	2	-	-	-	-	-	65	For pickling a thick layer of oxides or scale
2	-	11	-	10	-	-	-	65	For pickling a thin layer of oxides
3	-	-	-	10-20	1-3	-	-	20	idem
4	-	-	-	6	4	-	-	55	"
5	-	2-3	-	7-8	-	0.2	-	20	"
6	10	-	20g/l	-	-	-	20 g/l	70-75	"
7	6	-	-	10	50g/l	-	-	20	"

Descaling in alkalis and sodium hydride. Caustic sodium and potassium dissolve iron oxides without attacking steel. N. F. Lashko suggested the use of alkaline aqueous solutions for isothermic hardening of steels to develop high hardness, quenching being associated with a removal of the oxide film. Other proposals involve isothermic heat treatment in a bath of molten alkalis.

Foreign matter left on the surface of steel parts, may be removed due to the ability of sodium hydride to reduce iron oxides according to the reaction



This method has certain advantages as compared with usual pickling /21/. Acid pickling causes appreciable losses in metal (up to 2-5 %), and a rapid destruction of the pickling equipment.

The pickling bath used for surface cleaning contains molten anhydrous caustic soda to which a quantity of 2 % sodium hydride has been added. The working temperature of the bath is 350-370° C.

Duration of holding the parts in the bath depends on their size and the thickness of the oxide film, usually varying from 5 to 20 min. Flakes of chemically reduced scale on parts of mild steel may be removed by a water jet. After pickling, the parts are brushed in hot water to remove residues of NaOH, and then they are dried. A particularly clean surface may be obtained by subsequent immersion in acid solutions (for a period of 30 sec-5 min).

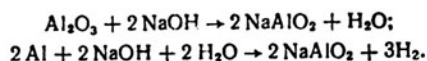
When stainless steel parts and parts of steel alloys containing a large percentage of chromium are treated by this method, the oxides, formed on

the surface will be incompletely reduced; they are in the form of powder and may easily be removed by dipping in water.

The hydrogen-sodium cleaning process may be applied to metals which resist the action of caustic soda at temperatures above 370° C viz: iron and its alloys (including cast iron), stainless and other alloyed steels, copper, nickel, chromium, titanium, and most of their alloys /22/, /23/. The process cannot be applied for cleaning such metals as zinc, aluminum, tin, and their alloys.

The use of this process does no harm to the surface after prolonged holding in the bath, since during that reaction no atomic hydrogen evolves which could diffuse into the metal to be cleaned. Besides, the bath does evolve any poisonous vapors.

Oxide removal from aluminum and its alloys by pickling. Aluminum and aluminum oxides are easily dissolved in aqueous solutions of caustic soda, thereby forming a soluble sodium aluminate NaAlO_2 and hydrogen according to the reaction:



Hydrogen does not evolve so long as the oxide film is not removed. After the reaction between the alkali solution and aluminum has started, a more or less violent evolution of hydrogen bubbles take place.

Usually the pickling baths contain from 50 to 160 g/l NaOH; their working temperature varies within the limits of 60-95° C. The pickling rate depends on the concentration of the solution, on the temperature of the bath, and also on the composition and condition of the metal or alloy subjected to pickling (e.g. heat treated, cold hardened etc) /24/.

Ordinarily, pickling of aluminum alloys prior to soldering is carried out in baths of the following composition: 1) 20-35 g/l caustic sodium NaOH; 20-30 g/l sodium carbonate Na_2CO_3 and the remainder, water; working temperature of the solution is 40-55° C; duration of pickling, 2 min; 2) 10% caustic sodium and 90% water; temperature of solution, 20-40° C; duration of pickling, 2-4 min.

Pickling is followed by rinsing the parts first in warm running water, (25° C) and then in cold water with subsequent clarifying (for 2-5 min) in a 15% aqueous solution of nitric acid. Again rinsing in cold water and drying at minimum 60° C until all traces of moisture are removed.

Oxides from the surface of cast aluminum parts may be removed by pickling in a solution of nitric and anhydrous hydrofluoric acids.

Oxide removal from magnesium and its alloys by pickling. Removal of oxides from magnesium and magnesium alloys is done in aqueous solutions of chromic anhydride of the following composition: 1) 20-30 g/l at a working temperature of 60-70° C and a pickling time of 8-12 min; 2) 150-260 g/l at a working temperature of 15-30° C and a duration of 8-12 min.

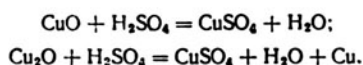
Pickling is completed by thorough rinsing in hot (50° C) running water, followed by rinsing in cold water, and drying. Before soldering, local cleaning with steel brushes, file or shaver is advisable. The surface thus prepared may be subjected to soldering, 2-5 hours after cleaning.

Pickling baths composed of aqueous acid solutions are also applied;

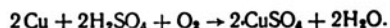
they have the following composition: chromic acid (H_2CrO_4), nitric acid (HNO_3), and hydrogen-fluoric acid (HF). Magnesium may be pickled in solutions containing orthophosphoric (H_3PO_4), sulfuric (H_2SO_4) and acetic acid (CH_3COOH).

Oxide removal from copper and its alloys by pickling. In open air, oxygen attacks easily the surface of copper and its alloys, even at low temperatures, forming oxide films.

Most frequently pickling of copper and its alloys is done in an aqueous solution of 10% sulfuric acid H_2SO_4 , which promotes loosening and dissolving of oxides films without attacking the base metal. The process takes place according to the following reaction:



If the pickling solutions contain some quantity of deoxidants (dissolved oxygen, nitric and chromic acids), copper also may be involved in the reaction:



Copper and its alloys (brass and bronze) are pickled in aqueous solutions of the following composition: 1) 0.5-5% H_2SO_4 ; 2) 0.5-10% HCl ; 3) 1-5% H_3PO_4 .

Pickling may be done also in mixtures of concentrated sulfuric and nitric acid, with subsequent triple rinsing in cold water.

Sometimes the surface of copper and brass is submitted to a double pickling in two solutions: 1) for 1-2 min, in a solution composed of 10% H_2SO_4 , 5% potassium bichromate and the remainder, water; 2) in a solution of 20-30 g potassium or sodium cyanide and 1 l water. After pickling, the parts are rinsed in cold water, and after drying in sawdust again rinsed in hot water (at 70-80°C). Sinter, deposited on parts prepared for soldering, may be removed by dipping in hydrochloric acid with subsequent rinsing and drying.

Removal of nickel oxides by pickling. The compact oxide films formed on nickel when exposed to atmospheric influence, afford a good protection from further oxidation.

Oxides formed during annealing are chemically stable, and therefore they are difficult to remove in acid solutions. In order to remove oxide films from nickel and its alloys, various solutions of nitric acid, bichromate mixtures with sulfuric acid may be used. One of these solutions, e.g. has the following composition: 1000 cm^3 H_2O , 1500 cm^3 H_2SO_4 (specific gravity 1.87), 2250 cm^3 HNO_3 (specific gravity 1.36) and 30 g NaCl .

Before pickling, the parts involved are held in hot water and then immersed in the pickling bath; after pickling they are rinsed in hot water. Duration of pickling is 5-10 sec. Pickling and rinsing are followed by neutralization of residues in a 1% aqueous solution of ammonia and by drying in hot water or in sawdust /25/.

Oxides formed on nickel alloys, and having a relatively high chemical stability in acids, are removed by means of aqueous solutions of nitric and hydrofluoric acids) combined in the following proportion: 10-20 % HNO_3 ,

4-8 % HF and the remainder, water.

Removal of tungsten oxides by pickling. Pickling of tungsten parts prior to their soldering may be made in different ways: by immersing in liquid caustic soda or through electrolysis in a 5 % solution of caustic soda (NaOH). The second method is suited for pickling tungsten wire /26/; in the electrolytic method, the tungsten parts serve as an anode, the cathode being formed by nickel. Pickling and rinsing in water is followed by electrolytic neutralization in a weak solution of HNO_3 .

Removal of lead, tin, and zinc oxides by pickling. Oxides formed on the surface of lead and tin may be dissolved in aqueous solutions of hydrochloric acid (1:1).

Zinc oxides may be removed by pickling in diluted solutions of sulfuric or hydrochloric acid or of their mixtures, e.g. in a solution compounded of 1 part concentrated H_2SO_4 , 1 part concentrated HNO_3 and 10 parts water. Pickling is carried out at room temperature, for 1 min.

Pickling may also be done in a solution composed of 225-300 g/l CrO_3 , 15-30 g/l Na_2SO_4 , 10 H_2O . In this solution a momentary pickling is carried out, assuring a bright surface of the zinc and zinc-alloy parts /25/, /26/.

Removal of silver and gold oxides by pickling. Oxide films formed on gold and its alloys are removed by dipping in a solution of aqua regia (3 % HNO_3 , 7 % HCl and 90 % water). Silver oxides may easily be removed by pickling in a 50 % aqueous solution of HCl at a temperature of 20° C.

Removal of titanium and titanium-alloy oxides by pickling. Upon heating, titanium and its alloys form superficial oxide films TiO_2 (rutile) firmly adhering to the base metal. Beneath the oxide film an interlayer is formed which is rich in oxygen and nitrogen, both absorbed from the air during heating. This interlayer has a low plasticity, leads to embrittlement of the base metal and in numerous technological operations (e.g. welding, stamping, etc) it is liable to promote destruction. Oxygen and nitrogen stabilize the α -solid solution of titanium; therefore, this interlayer is sometimes also termed alpha-layer.

Heating above 650-700° C is liable to cause a particularly strong oxidation of the surfaces of titanium parts. Therefore, parts or stocks from that metal or its alloys, subjected in an air medium to heat-treatment, rolling or other operations, form on their surface firmly adhering, chemically stable, scale films. In such a case preparation of the metallic surface may be performed by a combined method consisting of preliminary sandblasting of the surface (at an air-pressure of about 4 atm) and a subsequent chemical pickling. Sandblasting removes only scale without destroying the gas-saturated alpha-layer existing beneath the scale film; apart from this, sandblasting favors formation of a superficial metallic film enriched with silicon oxide.

Solubility of titanium oxides depends on the temperature at which they are formed /28/. Titanium and its oxides are soluble in many acids. Dissolution takes place most intensely in hydrofluoric acid and to a smaller

extent (in the sequence of solubility) in hydrochloric and sulfuric acid. Nitric acid, being a strong oxidizer, causes formation of a protective oxide coating on the surface of titanium, thus strengthening its corrosion resistance. In a large concentration, sulfuric acid causes passivation of titanium. In order to remove the oxide film and the alpha-interlayer from the surface of titanium and its alloys, various solvents have been suggested. In some of these solvents composed of mixtures of different acids, the poisonous fluoric acid has been replaced by sodium fluoride.

A reliable pickling method used after sandblasting, has been devised by V. P. Batrakov and E. M. Timonina; this method involves a solution of the following composition: 34-35 ml HCl (specific gravity 1.19), 55-60 ml HNO_3 (specific gravity 1.4), 50 g/l NaF and the remainder, water. Pickling may be accomplished at room temperature (for 5-10 min) and also at a temperature of 45-55° C (for 10-30 min). After pickling, the metallic surface is rinsed in hot water (40-50° C), rubbed with hair brushes and dried in a current of hot air in a drying oven at 100-120°C for 10-15 min.

At a reduced thickness of the oxide film, pickling of titanium and its alloys may be done in solutions of sulfuric acid or in a hot solution of tetrafluoroboric acid $\text{H}(\text{BF}_4)$.

Parts covered with a thick scale-blanket should be pickled in a mixture of nitric and hydrofluoric acids. In order to avoid hydrogen-saturation of the surface of titanium parts during the pickling process, an aqueous solution of 15 % HCl, 5 % HNO_3 and 5 % NaCl may be used (according to V. P. Batrakov).

Titanium parts covered with a thin film of oxides, should be pickled in an aqueous solution of nitric and hydrofluoric acids, prepared in the following proportion: 20 % parts by volume of HNO_3 , 1 to 3 % (p. b. v.) of 40 per cent HF and the remainder, water. This solution attacks both the oxides and the titanium base.

A stronger pickling action may be achieved with an aqueous solution of hydrochloric and hydrofluoric acids; its composition may be for example, 15 % parts by volume HCl, 3-5 % HF and the remainder, water. This solution, while acting on oxides, attacks also the base metal, and in prolonged pickling it is liable to cause local corrosion of titanium. Thick oxide-layers may be dissolved in a mixture of 96 % NaOH and 4 % NaNO_3 , molten at 500° C. This mixture, though dissolving titanium oxides, does not attack the titanium base-metal. Removal of titanium oxides may be done efficiently also in melts of caustic soda and sodium hydride (98 % NaOH and 2 % NaH) prepared at 370° C /30/.

Electrochemical descaling of steel parts. The electrochemical method of descaling is very convenient in mass production and in instances requiring rapid surface-cleaning. Generally, this process may be divided in several steps /31/: 1) degreasing; 2) surface cleaning; 3) removal of oxide and scale films associated with simultaneous tinning (for 3-5 min in a bath); 4) rinsing in cold water through immersing; 5) removal (if necessary) of the tin coating; 6) rinsing in hot water (90° C).

This procedure is mainly used for steel parts and involves two operations: removal of scale and depositing a tin coating on the cleaned surface.

A tin blanket is sometimes useful as a technological interlayer (base) for cases of soldering with low-melting solders. Moreover, tin prevents rusting of steel.

In this method, degreasing is usually done in solutions or in alkaline baths (preferably of the anodic type) at a voltage of 4-10 v and an amperage of 6.5 amp/dm^2 . The bath temperature is close to the boiling point of the solution with a concentration of 100 g alkalis.

In order to remove scale and oxides from the parts, they are immersed in a bath of H_2SO_4 , containing the requisite amount of tin entrapped by the tin anodes. Small amounts of special additives are included to increase conductivity of the pickling bath /31/. The anodes of the bath consist of high-silicon iron and are placed parallel to the tin anodes. Duration of immersing is 30-60 sec; if necessary, the tin coating may be removed from the surface of the parts.

Formerly, instead of acid pickling, the electrolytic caustic method has been employed for cleaning the metallic surfaces prior to galvanizing. In this method, the parts to be cleaned, serving concurrently as a cathode, were immersed in a bath of molten caustic soda heated up to $427-538^\circ \text{C}$. Sodium, in precipitating on the surface of the cathode (of the parts respectively) deoxidizes the scale layer; as a result, easily removable sponge iron is formed. One of the basic difficulties of this method comes from the necessity of a uniform distribution of the current intensity, which in instances of batch operation, is rather complicated. Besides, this method is unsuitable for stainless steel parts, due to the high resistivity of the latter /32/-/34/.

§ 4. Tinning and Metal-Coating of Parts

In soldering of certain metals or alloys coated with stable oxide films, the methods of removal ordinarily used during soldering (e. g. fluxing, removing in an atmosphere of reducing or inert gases) may prove to be insufficient. In such instances, in order to assure proper penetration of the molten solder into the gap between the parts, a preliminary thin layer of metal or solder may be applied on the surface of the parts to be soldered, on which less stable oxides form during soldering.

Metallic coating may be applied on the surface of parts by various methods: tinning with molten solders, electrolytic coating termed also electroplating, metallizing, cladding, hard facing, etc; each of these methods has its own peculiarities, which are decisive factors in selecting the proper plating method.

Preliminary coating of the surface with metals or soldering alloys is also necessary in cases where direct soldering of two metals or of metals and alloys to a ceramic base is in general impossible. In certain cases, several superposed metallic layers may prove to be necessary. So, for instance, steel parts covered with an electroplated silver coating, should not be subjected to soldering, since, as a result of the absorption of oxygen by silver, the steel parts are liable to be oxidized during soldering and to get a porous structure. Porosity during soldering may be avoided by a preliminary coating of the steel parts, first with a copper, then with a nickel layer and finally with a silver film /35/.

The quality of soldered joints consisting of nickel alloys and steel having a large amount of chromium, aluminum, and titanium, may be

improved by coating the surface prior to soldering, with a nickel or a nickel-copper layer.

Electroplating with chemically pure tin is very often of poor quality since the tin layer has a reduced corrosion resistance in organic acids and, upon prolonged exposure in open air, it impedes the process of soldering.

At low temperatures, the electroplated tin layer easily changes into gray tin /36/.

Special electroplating baths and working conditions have been devised e.g. for applying a layer of tin-lead solder (60 % Sn and 40 % Pb) on metallic parts. The electrolyte involved is a mixture of tin and lead fluorides /37/.

The tin layer maintains its effectiveness, i.e. its suitability for soldering, even after prolonged storage. In tinning various alloys, the minimum thickness of the tin layer depends on its interaction with the base metal. The following layer thickness should be used /38/ : 0.0050 mm for tin on steel parts; 0.0075 mm for tin films on copper and 0.0100 mm for tin layers on brass.

After prolonged storage, tin-lead solder-coatings (30 % Sn) 0.0050 mm in thickness, deposited from a fluoborate electrolyte, proved to be more stable than pure tin layers.

Tinning of small steel, copper or brass parts (e.g. pins, hooks, tags, etc) may conveniently be done by reducing tin from a solution of tin salts. For that purpose, the parts are immersed in an aqueous solution of tin salts and subjected to boiling for several minutes. The thickness of the deposited tin layer is 0.00025—0.0005 mm. In the course of time, such a layer loses its effectiveness but it may be restored by new tinning.

Reactive tinning in a hydrogen atmosphere at 500° C with tin chlorides /38/ and also with liquid tin chlorides and bromides, or their mixtures with chlorides of heavy alkaline metals, may also be applied in tinning steel, copper or brass parts. Tinning of titanium and its alloys by this method is carried out in an atmosphere of inert gases.

Copper plating of austenitic stainless steel parts, permits us to use in cases of soldering with tin-lead solders, protective or less effective fluxing agents (e.g. solutions of colophonium in ethylic alcohol, or the LK-2 and LTI-120 fluxes).

Copper, nickel, molybdenum or chromium coatings applied on titanium parts, develop a weak bond with the surface of the base metal and are easily removed from it. To assure a better bond, prior to electroplating (with Cu, Ni, Mo, Cr, etc), these parts are to be coated primarily with a zinc layer /39/. To do this, the parts are reactive-tinned with ZnCl_2 -containing fluxes or by galvanizing in a bath of the following composition: 200 ml HF (40 %), 100 g ZnCl_2 and 200 ml ethylene glycol.

Electrolysis in the bath of the above composition is achieved within 50 min after immersion, at a temperature of 20-26° C at a voltage of 6 v and an amperage of 1 amp/dm², graphite serving as anode. The zinc-coated titanium surface constitutes a good interlayer for subsequent applying of other metallic coatings.

The metal-spraying process may be applied to either pure metals or metallic alloys. Its disadvantage consists in the fact that, during the transfer of metallic droplets on the surface to be metallized, the droplets may be subjected to an intense oxidation. As a result the applied layer includes in its composition a relatively large amount (up to 30 %) of its own oxides. This procedure is more suited to self-fluxing substances.

Coating of metals and alloys by the so-called electrical spark method has little effectiveness and yields layers with a thickness no more than 5-10 mm.

Largely used in soldering, is the method of applying a layer of hot molten solder on the surface of metallic parts. Since this method initially involved tin and tin-lead solders for coating purposes, it was termed "tin-ning". At present the term "tinning" refers generally to hot coating of metals and alloys with solders of different composition.

Most commonly used are tinning methods by sweating and hot dipping (immersing). In certain cases the method of reactive tinning may be used.

Hot dipping (or dip soldering) of parts may be done by immersing them in molten flux followed by dipping in a bath of molten solder. Those portions of the parts, which should be free from tin layers, may be preliminarily coated with graphite or a mixture of chalk and water glass; before immersing in the bath, this layer should be thoroughly dried.

Prior to tinning, the surface involved should be cleaned of dirt, grease, oil, scale or oxides.

Hot sweating with tin-lead solders may be achieved in the following manner /39/. The part to be hot sweated, is covered with flux and then heated to a temperature slightly above the melting point of the soldering alloy. Heating may be done with soldering torches, in electrical coils, in furnaces, etc. In tinning steel or copper, the flux used is ordinarily an aqueous solution of zinc chloride. When the zinc chloride applied prior to heating starts to boil, the solder, on which ammonium chloride is applied concurrently, is spread on the surface to be tinned. After cooling, residues of flux are removed by rinsing in water; the layer is then thoroughly dried. When tinning small areas the solder may be applied by means of a usual soldering iron (see Chapter VIII).

Tinning of steel, copper and copper surfaces, may sometimes be done with a special paste /40/. Usually the paste required for tinning metallic parts prior to soldering, is a compound of finely ground soldering powder (most frequently POS40, POS61), flux, water or alcohol. The following is a paste composition* used in preliminary tinning of steel parts: 1 part of a mixture containing 30 % crude alcohol, 45 % technical glycerine, 18 % saturated aqueous solution of ammonium chloride, 5 % aniline hydrochloride and 2 % triethanolamine (an inhibitor, reducing the corrosivity of the fluxing residues), and 6 parts of soldering powder POS40 or tin (granulation of the soldering powder equals 100 mesh).

Prior to soldering, the tinning paste is applied on the previously cleaned and degreased surface by means of a brush and then heated with a soldering torch. Residues of flux are to be removed.

Layers of low-melting tin-bearing molten solders may be applied on aluminum and its alloys by mechanical means (the surface of the parts are cleaned of oxides with a steel brush or with a cutting tool), by ultrasonic soldering bits or by abrasive methods.

Dip soldering of parts by immersing in molten tin or tin-lead solders has the following essential disadvantage: the applied layer is non-uniform in thickness and, as a rule, has a certain porosity, which assists in corrosion. In order that residues of molten solder be removed from the surface, it may be cleaned by centrifuging or by rubbing with a rough rag.

* The paste was proposed by I. S. Goneharov.

In some industries, e.g. in the manufacture of condensers, the process of tinning with tin-lead solders has been mechanized, thus improving efficiency of the process, and the quality of coating, and saving lead. Parts tinned by this method exhibit a smooth coating of uniform thickness, regardless of their shape or size /41/.

Mechanization of tinning is carried out in the following way. The parts to be tinned, after cleaning, fluxing in a solution of zinc chloride, and drying, are inserted in a container which in turn is introduced into a cast iron crucible filled with molten solder. Steel and iron parts are kept in the bath for 13-15 sec, copper and brass parts, for 10-12 sec. The melting point of the solder (POS61 or tin solder) should vary within 390-410° C. The elevated temperature is an indispensable condition for a thorough heating of the parts prior to their centrifuging. Upon withdrawal from the crucible, the container is subjected to sudden shaking and then quickly fed into the receiver of the centrifuge; the latter is covered, and the container together with the parts is rotated for 6-8 sec at a speed of 110 rot/min. Due to the centrifugal force, small droplets of excess solder are thrown to the inner walls of the centrifuge, where they are gathered on the bottom of the collector. The tinned parts are fed into a bath with a hot-soda solution for their neutralization (at 60-80° C). After neutralizing, they are rinsed in cold running water and then in pure hot water and finally dried in a drying oven at 8-100° C.

Once in 1.5-2 hours, the surface of the tinning bath, covered with oxides (due to the elevated temperature of the process) should be cleaned by means of graphite powder which is applied on the walls of the container and removed from it after 10-15 min. In those tinning baths where the oxides have not been removed, after tinning, the parts exhibit a color-oxide film (temper colors) which is to be removed by immersing for 5-8 min in aqueous solution of zinc chloride.

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Chapter VIII

SOLDERING WITH SOLDERING BITS

The soldering bit (also termed soldering copper or soldering iron) is used in the soft soldering of metals, for heating and melting the solder, and for applying it to the parts to be soldered, concurrently heating the seam area. At present, the soldering bit is used also to clean the oxide films from the parts to be soldered and to assure automatic feeding of solder and flux.

The soldering bit is a metallic rod (usually of copper), one end of which has a special shape to facilitate filling the gap with molten solder and heating the base metal to the requisite temperature; the other end is fastened to a steel rod provided with a handle of wood or another nonconductive material.

The soldering bit may be heated either intermittently as it cools, or continuously by a source of constant heat which keeps the temperature of the bit within definite limits. Heat transfer from the bit to the parts to be soldered occurs through the layer of molten solder; the latter assures an intimate heat contact between the bit and the part to be joined, serving concurrently as a heat source for that part of the work to be soldered, which is close to the molten solder. The rate of heat transfer from the soldering bit to the molten solder and to the work, depends upon the thermal conductivity of the soldering bit, of the solder, and the parts to be soldered; it depends also on the temperature of the soldering bit and the size of the area of contact between the solder and the parts to be soldered. In soldering, the temperature of the soldering bit is the more stable, the heavier the bit. Therefore, with a greater weight of the soldering bit, the efficiency of soldering increases due to the reduction in time required for preheating the bit; at the same time the quality of the soldered joint is improved.

The amount of heat required for a thorough heating of the seam area increases with the increase in weight of the soldering bit. (Figure 74). Therefore, a heavy bit permits us to solder large-sized parts. However, manual soldering imposes certain limits on the weight of a bit (usually the weight varies from 250 g to 1 kg and seldom attains 2 kg) /1/. Heavy soldering bits are more difficult to handle, thus limiting the sizes of the parts to be soldered. Usually, a soldering bit is employed for small parts only. Sometimes, when a soldering bit is used, the parts to be soldered are preheated by external heat sources so that they may be slightly increased in size.

Most frequently, soldering bits are made of technical high-conductive copper. Copper used for that purpose should have a high degree of purity

(a minimum amount of impurities, particularly hydrogen). Such soldering bits are less subjected to wear during soldering. Copper soldering bits dissolve relatively early in lead solders.

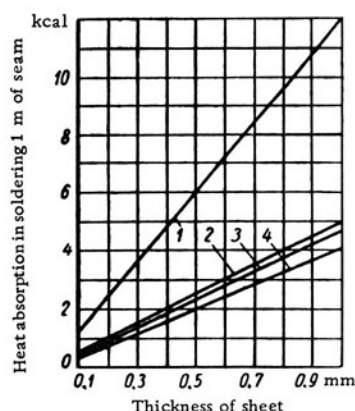


Figure 74. Heat absorption in soldering 1 m of seam when joining various metals (according to Voigt and Wertheim):

1—copper; 2—zinc; 3—brass; 4—sheet metal.

By adding 1% Cr to copper, the solubility of the soldering bit while immersed in molten tin-bearing solder may be reduced [2]. The main disadvantage of copper bits is their tendency to oxidize when heated. In that connection a great many patents have been registered, suggesting different methods for reduction of oxidability of copper bits during soldering [3]. One such patent proposed complete or partial replacement of copper with other metals, whereas some patents suggested coating the bit of the tool with a metal layer to protect the copper from oxidation. So, for instance, instead of copper the use of soldering bits fabricated from nickel or German silver was recommended. Such soldering bits are particularly suited for soldering with zinc-containing solders, since zinc has a particularly strong dissolving effect on copper. Soldering bits of low-oxidable bronze also have been used. Some authors suggested using soft iron for soldering bits but, as soft iron has a reduced thermal conductivity, it proved to be more practical to use hollow iron-rods provided with a copper core (Figure 75). Among the metals used for shielding copper bits from oxidation, nickel, nichrome, and silver should also be mentioned.

Most commonly used are soldering tools, the bit of which is sharply pointed or has the shape of a hatchet. Sharp pointed soldering bits are suitable for soldering parts intricate in shape. Among soldering bits, very popular are cylindrical bits which assure minimum heat losses and therefore a maximum heat transfer from the bit to the part to be soldered. Figure 76 shows some shapes of modern soldering bits. The working face of the soldering tool (the bit proper) has a grooved or pointed end.

With the increase in thermal conductivity and weight of the parts to be soldered, the weight of the soldering bit should be increased too. In soldering copper parts, the bit should be heated faster than in soldering parts of the same weight which are made of steel.

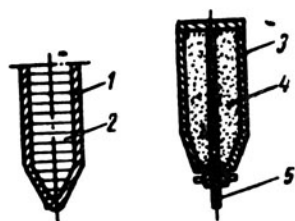


Figure 75. Cutaway view of hollow-shank soldering bits:

1—cast-iron hollow shank; 2—lead; 3—soft-iron hollow shank; 4—sand; 5—copper lamella (bit).

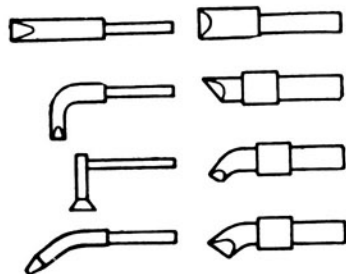


Figure 76. Various shapes of soldering bits.

The oldest method of heating the soldering bit is heating in an open flame. For that purpose various solid, liquid, or gaseous fuels are used (charcoal, kerosene, town gas, etc.). Coal is unsuitable since the sulphurous products of its combustion cause diffusion of sulphur into copper, thus impeding tinning of the bit with molten solder. Heating of the soldering bit may be conveniently done also in electrical furnaces or in a bright non-smoking (sootless) gas flame.

Figure 77 illustrates a type of electrical soldering bit, of intermittent action, devised by I. V. Ilinin. According to this author, the soldering bit is heated by the electric arc generated between a coal rod inserted inside the shank of the tool and the body of the soldering bit. The current is fed to the soldering bit through the contacts 4 and 5 so that in the soldering bit placed between them, the coal rod will be connected through the holder 2 to one phase, whereas the body of the soldering bit will be connected to the other phase. In order to generate an electrical arc between the coal rod and the soldering bit, the coal rod should be slightly rotated. Heating of a soldering bit 1 kg in weight, to 500°C, at voltage of 24 v is achieved within 3 min; power consumption of such a soldering bit is 1.5–2 Kw.

For soldering very irregularly shaped parts having semi-accessible places, e.g. dentures, a special pencil-shaped soldering bit has been devised. It consists of an iron shank with a bit made of copper-tellurium alloy, and of a separate steel part which includes a special coil for heating the bit up to

141.

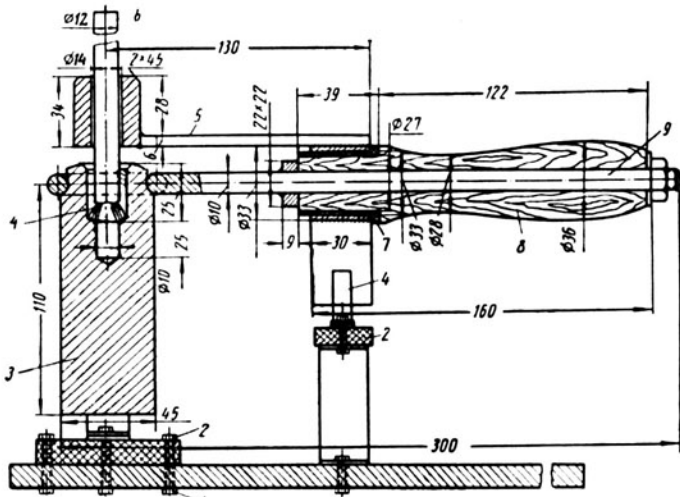


Figure 77. Conductor-less electric-arc soldering iron:

- 1-screw; 2-marble holder; 3-soldering bit;
4-contact for arcing; 5-holder of the carbon rod,
(other contact); 6-carbon rod; 7-insulating bushing;
8-handle; 9-rod of soldering iron.

Duration of intermittent heating of the bit before soldering is 2-3 times longer than the time of the main soldering operation, due to the preheating involved.

In order to make up for heat losses during soldering, it is advisable to heat the bit by a continuous heat source. At present continuously heated soldering irons are used very largely.

Continuous heating of the soldering bit may be carried out by burning liquid or gaseous fuel. Usually liquid fuel (gasoline or alcohol) is employed. Continuously heated soldering tools consist of a fuel reservoir, a torch, and a soldering bit. Figure 78 shows a gasoline soldering tool. The heating part of this tool is similar to the soldering lamp but the gas flame heats only the bit and not the solder or the parts to be soldered.

Continuously heated soldering tools do not need any hoses or conductors which may impede working.

Most commonly used as gaseous fuel for continuously heated soldering tools, are producer (illuminating) gas, acetylene, or hydrogen. In such cases the soldering tool consists of a gas torch and soldering bit. Heat is generated from a mixture of air and gaseous fuel, the air being fed through a hole in the air-suction pipe.

The soldering bit heated with producer gas affords greatest safety, and is therefore preferred to acetylene or hydrogen heated soldering tools which should be used only when producer gas is not available.

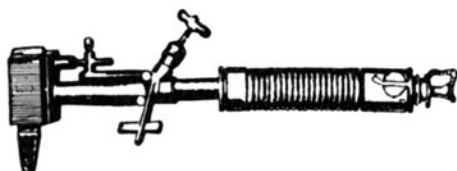


Figure 78. Gasoline soldering tool

Continuous heating of soldering bits may be achieved also through the alumino-thermic reaction but this method did not find any wider use /3/.

Very popular are electrical soldering bits. Such tools have a lighter weight than intermittently or continuously heated soldering tools using liquid fuel. Usually, electrical soldering tools are composed of a copper rod heated by a hollow ceramic tube and a nichrome resistance-coil (heating element) inserted into the latter, and designed for a definite voltage and temperature. The heating element may be placed either outside the working part of the tool (externally heated soldering bits) or inside a chamber through which heat is transferred to the bit (internally heated soldering bits).

For soft soldering (with low-melting solders) in repair and assembling of radio-equipment an electric soldering bit may be used, in which the heating coil is wound on a mica plate separated from the rod by other mica plates, 0.5–0.3 mm thick. The winding of the heating coil is designed for 12 v; the output of the soldering tool is 20–25 w. Being fed with low-voltage current, this type of soldering tool is relatively safe in operation /5/.

Due to light weight, simplicity of operation, and absence of any combustion gases, electrical soldering tools present definite advantages; on the other hand, their main disadvantage is reduced life due to the frequent damage of the heating coil.

Preheating of the parts prior to their soldering with an electric soldering tool, is achieved with gas torches, electric heating elements, etc. So, for instance, in soldering terminals to conductors, preheating of the terminals is achieved by a heating element of 700 w. For this to be done, the terminal is placed on the heater and then soldered with an electric soldering tool of 250 w. This is a rather lengthy process: soldering of the terminal is completed in 30 min.

Tables 69 and 70 present basic characteristics of electrical soldering tools designed for 220 v. The working part and the groove of the bit are cleaned with ammonium chloride or with a file. On the bit cleaned in such a way, a layer of molten solder is applied, which is transferred to the seam. In order that the base metal be heated, the bit is passed over the surface close to the gap between the parts until the solder melts and fills it completely; concurrently, a convex bead is formed on the opposite part of the seam.

Various applications of electrical soldering tools are given in Table 70.

Overheating of electrical soldering tools may lead to premature damage of the bit, to a greater power consumption, and to waste of time in cleaning the oxides from the edges by means of a file, or with ammonium chloride. On the other hand a complete switching off of the soldering bit during operation, causes considerable cooling, thus involving greater power consumption

and time for new switching. In order to check the degree of heating of the bit, certain electrical soldering tools have built-in thermocouples, the ends (junctions) of which are connected to a millivoltmeter /7/. Other improvements consist in that an additional resistance connected to the electrical heater of the soldering iron, automatically prevents overheating of the soldering bit /8/. Certain types of electrical soldering tools possess especially designed windings assuring a fairly constant temperature of the working tool for several hours. In certain electrical tools, feeding of the liquid or solid solder is done automatically. In such tools, the wire-shaped solder is fed to the soldering bit /9/. The amount of molten solder fed to the seam may be controlled by a limiting device which prevents excessive melting of the solder on its heated end. The amount of wire-shaped solder fed to the bit is controlled by means of a brake connected to a micrometer. Control of dosing of the solder is achieved with a micrometer /9/.

Table 69

Characteristics of electrical soldering tools

Weight of the tool without conductors, in g	Diameter and size of copper bit, in mm	Output in w	Duration of heating, in min
110	6	55	2.5
220	6 × 15	110	2.75
530	22	125	2.25
850	26	265	5.0
1000	20 × 40	355	12.0

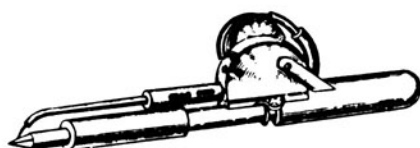


Figure 79. Electrical soldering tool with automatic feeding of the wire-shaped solder

Electric soldering guns are also fitted with a feeding control of the wire-shaped solder, the soldering wire, led to the bit through a special tube, is unwound from a bobbin placed above the handle of the tool /10/.

In order to save expensive silver used in silver-soldering work, another method of feeding the solder has been devised: powder-like solder is gravity-fed (through a tube from its container), to the soldering bit, the places to be joined being previously covered with flux. This method was found to be satisfactory in soldering the blades of rapid centrifugal ventilators to the hub of the rotor. For this to be done, the solder from a stationary container was fed to the soldering area, while the hub is rotated uniformly in the appliance /11/. Sometimes, electrical soldering tools are fitted with electronic timing devices /12/. For soldering with low-melting solders, special

soldering machines are used with automatic feeding of the wire-shaped solder /13/.

Table 70

Characteristics and uses of electrical soldering tools /6/		
Applications	Diameter of the copper rod of the soldering bit in mm	Output of the soldering bit, in w
Soldering of small parts (radio- and electrical equipment, tools, etc)	6.2-10.5	44-52
Soldering of medium-weight parts (telephone and radio equipment, electrical instruments)	10-12.5	60-70
Fast soldering of medium-weight parts (telephone and radio equipment, electric instruments, etc)	10-13.5	85-100
Very fast soldering of radio equipment and electrical instruments	13.0-21.0	130-150
Very fast soldering of tinned thin wire	13-25.0	170-200
Soldering of tinned medium-gauge wire, ventilators, electrical parts, parts of planes, etc	25-34	225-250
Soldering of refrigerators, copper-plated and tinned heavy-gauge wire, parts of ships and planes, etc	28-34	300-350
Soldering of tanks, parts of large vessels, ventilators, fittings, etc	34	350-650

Many fluxes, used particularly in soldering aluminum and its alloys with low-melting solders, cause corrosion of the soldered joint; this fact led to a considerable improvement of the electrical soldering tools for fluxless soldering. In this case, removal of oxide films from the surface of the base metal is achieved by one of two methods: mechanical or ultrasonic destruction of the oxide film (see Chapter XIV).

Mechanical removal of oxide films is essentially an improved variety of the so called sweating method of soldering, the oldest of the fluxless soldering methods. The soldering bit of a modern sweating tool for low-melting solders has a built-in steel-wire brush which when subjected to vibrations, cleans the surface. The molten solder around the brush assures both protection from oxidation, and wetting of the parts to be soldered. The vibrating system of the unit has a speed of 10 rot/sec. Heating of the soldering tool is done by means of a heating element of 165 w/14/. Oxide removal from the surface of aluminum parts tinned with low-melting solders, may be accomplished also by means of a soldering tool fitted with a grooved bit /15/.

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Chapter IX

SOLDERING IN LIQUID MEDIA

In order to protect the parts to be soldered from direct contact with the air, they may be heated by immersing in a bath of molten salt or solder. Heating is thereby achieved due to the heat exchange between the metallic parts and the liquid bath, the temperature of which is raised to the working temperature of the soldering process. With this method, the heating rate is 3-6 times greater than the heating rate of the same parts in direct-heated furnaces /1/ (with an uncontrolled atmosphere). The layer of molten salt or solder prevents oxidation during soldering and cooling in open air after withdrawal of the work from the bath.

In this method, the full time cycle for operation seldom exceeds two minutes. Efficiency is very high as this method permits simultaneous rapid soldering of a large amount of parts, and easy mechanization of the soldering process.

Soldering in liquid salt-baths is widely used, particularly in soldering structural and carbon steels, copper, nickel, aluminum and their alloys. Soldering of steel, copper, nickel, and their alloys, with copper, brass, and silver solders may be done successfully in the salt-baths usually employed in heat treatment (for carburizing, cyaniding, etc). In soldering aluminum and its alloys, molten fluxes serve as the liquid bath. This method is more convenient than soldering in direct-heated furnaces since it affords more uniform heating and exact regulation of the soldering temperature within close limits.

The great heating rate in liquid baths permits considerable reduction of warping, crystal growth, decarburization, etc, of the metallic parts. The number of parts simultaneously immersed in the salt bath is limited by the volume of the bath and the reduction in the temperature of the liquid medium, which occurs as a result of heating of the immersed parts.

A great advantage of soldering in salt and flux baths is the opportunity to combine this method with hardening.

Most commonly used are soldering salt-bath furnaces of the following types: V-10, V-20 and V-30; the monophasic electrode bath-furnaces S-20, S-25 and S-45; the triphase electrode bath-furnaces S-35, S-75, etc.

Automatic heat control of the bath-furnaces is achieved by thermo-electric automatic EPD17—potentiometers.

§ 1. Soldering in Liquid Salt-Baths

Soldering in liquid salt-baths is carried out at temperatures 20-40° C higher than the melting point of the solder. Soldering of steel parts may be done in barium salt-baths, and also in baths composed of chlorides of alkali and alkali-earth metals, ordinarily used for heat-treatment operations in tool shops. Soldering of steel parts with brass solders may be simultaneously done with liquid carburizing and cyaniding of these parts /2/.

Since the heating time in salt baths is too short to assure removal of zinc from the brass solder, this solder may be replaced by L62 or L60 brasses, i. e. soldering may be performed at much lower temperatures thus reducing warping of the parts and saving copper and electrical energy consumption.

This method does not afford the required pre-fixing of the solder which is liable to be shifted from its place by the moving liquid medium; besides, soldering of parts having blind holes cannot be achieved because the molten salt, in filling the gap between the parts, impedes penetration of the molten solder. To avoid this, the parts are fitted with drain holes for the escape of air and molten salts.

Table 71 presents some data about salt baths used for soldering at various temperatures.

For soldering with copper or brass solders, salt mixtures are most frequently used, composed of 20-30 % NaCl and 70-80 % BaCl₂. Fused NaCl salts, sometimes used for this purpose, are less suitable due to their corrosive action and the evolution of dense vapors above the salt bath at the soldering temperature /2/.

Low-temperature soldering of brass and copper parts of evaporators and refrigerators, with PSr12, PSr25, and PSr45 silver solders may be made in baths of molten table-salt NaCl /3/.

When soldering steel parts in liquid baths containing 25-50 % sodium cyanide, as a result of carburizing and nitriding, the surface of the parts will be covered with a thin rigid metallic layer which makes machining very difficult. Therefore, prior to soldering in liquid cyanide baths, the parts should be machined to their final dimensions. After soldering in low-temperature cyanide baths, the work is to be cooled in air or in an oil bath.

Hardening subsequent to soldering should be applied only upon complete solidifying of the molten solder, since a rapid immersion of the apparatus covered with still unhardened solder is liable to cause splashing of the solder.

Carbon and structural steels may be soldered in salt baths without any fluxing agents, if copper, brass or bronze is used as a solder. In soldering with silver solders, a flux should be used containing a certain amount of fluorides /4/. For that purpose, prior to immersion into the bath, the parts to be soldered are fluxed in common furnaces or first dipped in molten flux or in an aqueous solution of flux, and then immersed in the salt bath. After treatment in an aqueous solution of flux, the work should be thoroughly dried (full removal of moisture), before its immersion in the soldering bath.

For soldering parts in cyanide baths, Muntz-metal solder (60 % copper and 40 % Zn) may be used.

In principle, salt baths may be classed according to the heating methods and the materials used for their preparation.

Table 71

Composition of salt baths used for soldering purposes

Composition of bath, °C						Melting point °C	Recommended soldering temperature, °C
NaCl	BaCl ₂	CaCl ₂	KCl	K ₄ Fe(CN) ₄	Borax		
22.5	77.5	-	-	-	-	635	665-1300
30	70	-	-	-	-	650	710-1300
22	30	48	-	-	-	428	485-900
30	65	-	5	-	-	510	570-900
33	-	67	-	-	-	510	570-900
22	48	-	30	-	-	550	605-900
-	50	50	-	-	-	595	655-900
45	-	-	55	-	-	655	-
100	-	-	-	-	-	800	-
-	100	-	-	-	-	962	-
10*	65	-	-	25	-	650	-
20*	75	-	-	-	5	-	-

* Composition of bath used for liquid nitriding simultaneously with brass soldering

At present, the direct-flame heating method of soldering baths is relatively seldom applied. Such baths work only at temperatures up to 800°C. Usually, heating is achieved by burning mazout, gaseous or solid fuel. The main disadvantage of such baths lies in the fact that heat losses during charging of the parts to be soldered are very slowly made up.

At present, heating of commercial salt baths is mainly done by electric current. There are two types of electrically heated salt baths: externally and internally heated salt baths in which the parts are heated by a current passing through the molten salt bath. In the latter case, current is fed to the bath through electrodes immersed in the salt bath /5/.

The crucible of the externally heated salt bath is made of sheet metal 20-30 mm in thickness, and can be used when the working temperature is 700° C. The low resistance of such crucibles to the corrosive action of the molten bath leads to frequent damage. Therefore, quite often, particularly at elevated working temperatures, the internal method of heating by electrodes immersed in the molten bath is preferred.

The crucible used in this method is a low-carbon cast-steel vessel with a wall thickness of 20-30 mm; it is placed on a refractory-brick base, and surrounded by a welded 6 mm sheet-jacket. The gap between the bath, the brick basement, and the jacket is filled with fire clay, and asbestos crumb. The bath has an inner lining of refractory (fire) clay /6/.

Cooling of the electrode holders is done by water running through special channels welded on to the electrodes. The latter, immersed in the molten salt bath, may be placed close to the crucible walls, but a fair clearance should be left between the electrodes. Such baths usually have metallic crucibles which create a small magnetic flux between the electrodes and the crucible.

The maximum magnetic flux occurs when the distance between the electrodes (~ 25 mm) is small, and the distance between them and the walls of the crucible is large. To avoid this, ceramic crucibles may be used.

In order to prevent short-circuiting of the electrodes coated with scale during operation, they should not touch the bottom of the salt bath. In certain types of baths, in order to improve blending of the molten solder, the electrodes are placed on the bottom of the crucible. Melting of the salts is connected with some difficulties due to the fact that the salts, while in a solid condition, constitute a sort of insulator. Therefore, the bath can start to work only if there will be a liquid melt of salts between the electrodes. For this purpose, before switching on the bath, it is to be filled with a small amount of molten salts or with molten iron salts picked up from the iron electrode-connecting bar which solidified in the bath during heating. In certain baths, preheating is accomplished by open flame.

In baths, in which the electrodes are placed along the walls or on the bottom of the crucible, the parts to be soldered are liable to be overheated due to the lower resistivity of the electrodes as compared with the molten salts; therefore, through these parts a high-current passes (according to Kirchhoff's law). Baths with suspended electrodes are free of this disadvantage since the electromagnetic flux between the electrodes, passing through the molten salts promotes levelling of the temperature between the salt melt and the parts to be soldered (Figure 80). Some characteristics of industrial salt baths with an electromagnetic flux through the melt, are given in Table 72 (according to /6/).

Table 72

Characteristics of salt baths with electromagnetic flux
passing through the melt

	Type of bath		
	S-20	S-25	S-45
Capacity (output) kg/hour	90	90	200
External diameter, mm	1100	1100	1100
External height, mm	2350	2350	2350
Dimensions of the working space, mm			
height	200	380	340
depth	460	475	600
Rated power, kw	20	25	45
Voltage at the electrodes, v	5.5-17.5	-	-

In electrical baths, only alternating current is used, since direct current is liable to cause electrolysis of the salts contained in the bath /7/. Figure 81 depicts an electrode-heated S-25 type salt bath used in soldering operations.

Before soldering, the parts should be thoroughly cleaned of dirt, oil, or scale, to assure a good job. For that purpose the usual methods of degreasing with solutions of gasoline, carbon tetrachloride, etc, may be employed.

Before silversoldering brass or bronze parts, they should be either manually fluxed with borax or immersed for 3-5 sec in a boiling saturated aqueous solution of borax /3/. Such a prefluxing is sometimes applied in brass-soldering of steel parts /8/, and also in soldering of stainless or heat-resistant alloys. In the latter case, borax may be replaced by the flux No 200.

Prefluxing of steel parts prior to soldering with brass solders is necessary when the surface of the parts has been poorly prepared or when parts with considerable differences in wall thickness /9/ are to be soldered.

Descaling of the surface is done mechanically, with emery cloth, etc. Parts made of ferrous metals may be soldered without any preliminary cleaning of the surface, using salt baths of the following composition:

- 1) 60-70 % BaCl_2 and 30-40 % borax; 50 % BaCl_2 , 40 % NaCl and 10 % borax;
- 3) 65 % BaCl_2 and 35 % boric acid /9/.

In order to prevent any changes in the dimensions of the parts to be soldered, they should be thoroughly fastened by wire or by special jiggling fixtures. As far as possible fastening appliances should not have any screwed parts. Sometimes for fastening of the work, one may resort to tack welding, drilling, pin jointing, punching, caulking. Mandrel fastening is not always suitable since it may impede penetration of the molten solder into the gap.

Prior to its immersing in the soldering bath, the ready assembled work is heated up to 120-150°C for removal of any traces of moisture; only after thoroughly drying it is dipped in the bath preheated to the requisite working temperature.

The optimum soldering temperature for copper parts is believed to be 1120-1130°C; for soldering of brass or silicon-manganese bronze, the soldering temperature ranges between 940 and 950°C. For soldering of copper and brass parts with silver solders, the following soldering temperatures are recommended: /3/ : 830-850°C for soldering with the PSr12 solder; 720-835°C for soldering with PSr25 solders, and 730-780°C for soldering with PSr45 solders.

Sometimes before complete immersion in the bath, the joints of the parts should be preheated to a temperature slightly below the melting point of the solder. This is adequate, e.g. when the wire-shaped solder is externally placed on the gap (see Figure 11, 1-9). In such a case, after complete immersion of the parts, the solder melts before the joint is heated to the required soldering temperature, running off from the gap. Preheating of the joint may be done by partial immersion of the parts for 1-2 min in a salt bath, in order to keep the solder above the level of the liquid bath. After the joint is raised to the soldering temperature, the parts are completely immersed in the bath. If a foil-shaped solder is placed in the gap between the parts to be soldered, (see Fig 14), the parts may be immersed at once /10/.

In order to ensure uniform heating of the parts and to avoid oxidation of that part of the work not immersed in the bath, soldering should better be done after complete immersion. Duration of soldering is controlled by a time relay.

In serial production, the soldering process is often mechanized. For instance, ready assembled parts are suspended on a rotating setup and immersed in the salt bath by means of a pneumatic foot lever /11/.

In the Riga bicycle plant a special conveyer has been devised for mechanization of the soldering process; this unit contains the following baths: fluxing-bath, six-electrode salt-bath, and a steam heated rinsing bath.

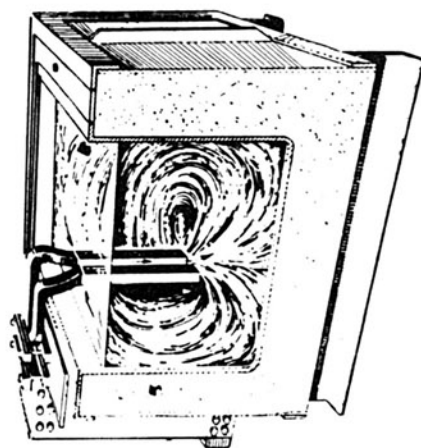


Figure 80. Cutaway view of an electrode-heated salt bath

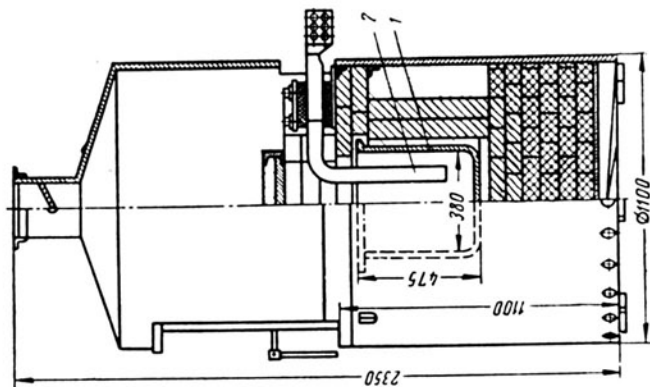


Figure 81. Diagrammatic representation of a S-25 type electrode-heated salt bath:
1 — bath; 2 — electrode

From the salt bath to the rinsing baths, the parts to be soldered are transferred on a chain conveyer moving with a speed of 0.4-1 m/s and provided with an electric drive of 1 kw /6/.

After soldering and cooling the parts to 200-250°C they are rinsed in hot water for removal of salt residues, and then dried in special ovens. Parts subjected after soldering to quenching in a water bath, need not be rinsed (after soldering).

Molten salts always contain a certain amount of oxygen and oxides which favor decarburizing of the steel parts during heating in the bath. In order to avoid decarburizing, and to assure deoxidation of the bath, a small amount of cyanides or silicon carbides are to be added to the bath /4/. Use of borax as a deoxidant (1-5 % from the weight of the salt) leads to a premature destruction of the ceramic lining of the bath. Therefore, after introduction of borax, it is recommended to add immediately fine-ground ferrosilicon in an amount of 25-75 % of the weight of borax, or to replace borax by sifted 75 % ferrosilicon, or by a 75 % ferromanganese powder added to the bath in an amount of 1 % of the weight of the salt. Usually, the bath should be deoxidized upon commencing work, and after 15-20 hours of operation /2/.

When nickel and its alloys are to be heated in salt baths, care should be taken to eliminate any traces of sulphur from the molten salt, since nickel and its alloys tend to form cracks in the presence of sulphur. In order to remove any traces of sulphur, the bath is charged for a period of two hours, (at the soldering temperature) with cuttings or clippings of nickel alloy.

During soldering, salt baths become impurified, chiefly with copper or zinc. At a high copper content of the melt (up to 0.2 %), the work is liable to be covered in the course of soldering with a thin copper tarnish. Therefore, in cases of periodical charging, the bath is to be cleaned every 24 hours by emptying it of the molten salts and filling with a fresh charge.

The excessive rise of temperature of the bath causes a black tarnish on the steel parts, and an intense red color of the brass parts. When the temperature of the bath is lowered below the rated limit, the soldered seam may not have a convex bead on the opposite part. In impure baths, the solder gathers to droplets, and the surface of the steel parts will not have its peculiar silver color.

When resoldering components, they are subjected to pickling and passivating for 4-5 sec in an aqueous solution containing 30-35 % of 75 % phosphoric acid, 20 % ethanol, 5 % butanol, 1 % hydroquinone, and the remainder, water. This treatment is followed by drying, applying the molten solder, and soldering in the bath.

Usually, only a single resoldering is permissible /6/.

The work taken out from the bath, is always covered with a thin salt layer which may easily be removed by rinsing. Salt is wasted not only as a result of its mechanical deposition on the parts immersed in the bath, but also as a result of its burning. This waste of salt should be compensated for by the following quantity: salts burned during a month's operation amounts to 5.5 % of the total weight of the salt charge; salt consumption for depositing on the parts, during 8 hours, attains a value of ~4-5 % from the weight of salt. Burning out of salts may be avoided by covering the surface of the bath with graphite or coal powder. To prevent evaporation of the salt, the bath is to be covered with a ceramic-lined cover. Charging of the parts to be soldered, is done through an opening in the cover.



Figure 82. Copper radiator soldered in a salt bath

Steel parts soldered in salt baths, with brass or copper solders, exhibit good mechanical strength, and no traces of overheating. The shear resistance (strength) of steel parts, soldered in salt baths, with different soldering alloys, is given in Table 73.

Table 73

Shear strength of steel parts soldered with different soldering alloys

Solder	Shear strength kg/mm ²	Source of infor- mation	Solder	Shear strength kg/mm ²	Source of infor- mation
Copper-phosphorus	10-12	/12/	Brass	30-35	-
Copper	30-35	/12/	Cast iron	12-27	-

The breaking load depends on the soldering method, a fact confirmed by the data presented in Table 74.

Soldering in salt baths is commonly used e. g., in the manufacture of bicycle frames, radiators, bushings for the drive of engine starters, foot levers of motor cars, brass wave-guides etc. Figure 82 illustrates the general view of a copper-radiator soldered in a salt bath. Salt-bath soldering may also replace welding in the manufacture of devices, hard alloy cutting tools /12/ etc.

Table 74

Breaking load of tubes soldered by various methods

Material and diameter of tubes in mm	Soldering method	Heating time-cycle	Heating temperature, °C	Breaking load, Kg
20-grade steel 18×14 20×18	Soldering with copper in electric bath-furnaces filled with molten borax	5 min	1120	7200
	Soldering with copper in electric bath-furnaces containing molten flux (35 % molten glass, and 65 % calcinated soda)	5 min	1120	7300
	Soldering with copper in furnaces containing molten flux (50 % glass, and 50 % calcinated soda)	5 min	1120	5300
	Soldering with copper in electric furnaces without flux	5 min	1120	5100
	Soldering with copper in salt baths	5 sec	1120	8000
25KhGSA steel 22×19 25×22	idem	10 sec	1150	6500
	idem	5 sec	1150	9500
	Welding	5 min		8400
	Copper soldering with borax in an oxy-acetylene flame	5 sec		9000
	Soldering with cast-iron solder in a salt bath	20 sec	1250	8200

§ 2. Soldering of Aluminum and its Alloys, in Molten-Flux Baths

Among the fluxes used in high-temperature soldering of aluminum and its alloys, the most popular are of the 34A type. Such fluxes are extremely active: they dissolve not only the oxide film formed on the surface of the aluminum or its alloys, but even the base metal (aluminum). Therefore, bath-soldering of thin walled parts with similar fluxes should be carried out with greatest care and precaution. Most suited for that purpose is the F-380 flux of the following composition: 50.5 % KCl, 38.1 % LiCl, 5.8 % AlF_3 , 5.6 % KF, or the flux No 17 with 51 % KCl, 41 % LiCl and the eutectic KF. AlF_3 *

* $\text{KF} \cdot \text{AlF}_3 = 46 \% \text{ KF} + 54 \% \text{ AlF}_3$.

(8%). These fluxes thoroughly dissolve the oxide film on the aluminum base and practically do not attack the base metal. With such fluxes, the soldering bath may work at a soldering range from 560 to 620°C.

The crucibles used in fluxing baths may be made of ceramics, stainless steel, or nickel and its alloys (inconel or monel metal). The auxiliary equipment and the fastening and soldering appliances should be made of the same metal in order to avoid impurifying of the fluxing bath with iron or copper compounds. When using fluxing agents, crucibles or baths may be made of aluminum or AMts—alloy sheets, 3-5 mm in thickness. The fluxing baths should preferably be heated by electrical heating elements placed around the crucible and thoroughly insulated against the action of flux vapors. For heating, the usual crucible electrical furnaces may be employed, in which the crucible containing the flux is to be placed. The fluxing baths must be provided with an exhaust hood. Certain types of baths with ceramic crucibles heated by means of suspended monel—metal electrodes have been described /13/.

The process of soldering aluminum and its alloys in fluxing baths covers the following basic steps: preparation of the surface, assembling, preheating, soldering, and removal of the residues of flux.

As in other methods of soldering aluminum—alloys, preparation of the surface of the parts to be soldered, consists in degreasing and removal of the thick oxide films from the surface. For that purpose, the work is to be treated (for 30 sec at a temperature of 80°C) with trichloroethylene vapors or with caustic soda. The parts and the solder are then immersed for 2-3 min in an aqueous solution composed of 1% HF, 1% HNO₃, and 98% water.

Other aqueous acid solutions (see Chapt. VII) may also be used for pickling purposes. For soldering, the wire, foil, or grain-shaped solder may be placed on the work and thoroughly fastened. In soldering of irregularly shaped parts, e.g., radiators or multilayer constructions, the silumin solder should be applied directly to the parts by cladding. For a sheet thickness of more than 1,6 mm, the thickness of the clad solder should be 5%; at a thickness below 1,6 mm, the thickness of the solder should be 10% of the thickness of the soldered part. Due to the low—plasticity of 34A or V62 low—melting solders in the cast condition, cladding of aluminum or its alloys with such solders is extremely difficult.

The gap between the parts to be soldered should vary within 0.05-0.12 mm, but should not exceed 0.25 mm; minimum length of overlapping is 6 mm, or about one sixth of the thickness of the thinnest section of the part /14/; for fastening of the work, the ordinary fastening methods or tack welding may be used.

Prior to the immersion in the molten—flux bath, the already assembled parts are to be dried and preheated to ~400°C in a direct—heated furnace. The time cycle of preheating should not exceed 5-15 min, in order to avoid strong oxidation of the surface, which may impede free flowing of the molten solder. Sometimes, gases, dissolved in the molten flux, are previously removed by mixing the bath with an aluminum rod or by dipping an aluminum sheet into the bath. If mixing of the flux is accompanied by fizzing, and evolution of gaseous bubbles, the mixing should be continued until this phenomena comes to an end. Only then, the bath may be charged with the preheated parts. Holding time in the bath for soldering is largely established by experiment, and usually varies within the limits of 30 sec to 3 min

depending upon thickness and weight of the work. Variations of the temperature of the bath should not exceed $\pm 5^{\circ}\text{C}$.

Solidification of flux on the surface of the parts leads to corrosion and therefore, any residues of flux on the surface of the soldered parts should be immediately removed after completion of soldering. For this to be done, the work is rinsed in hot (at $60\text{--}70^{\circ}\text{C}$) and then in cold running water; the parts are to be kept for 10-15 min in an aqueous solution of 2% phosphorous anhydride, then rinsed again in water, and dried at a temperature of $60\text{--}80^{\circ}\text{C}$.

Pickling of the soldered parts in an aqueous solution of 5-14% NaOH followed by clarification in a solution of 5-10% HNO_3 is less effective than prolonged rinsing in hot running water. In case of a poor soldering (except instances of burning), favorable results may be obtained after a triple resoldering /15/.

From time to time aluminum oxide deposited on the bottom of the crucible should be removed, and the bath refilled with a fresh salt charge.

§ 3. Soldering in Molten-Solder Baths

Soldering in molten-solder baths may be achieved by immersing the previously cleaned, degreased, oxidized, and thoroughly fluxed parts in the molten bath where they are tinned (covered by a layer of molten solder). The solder penetrating into the gap between the parts, upon freezing, forms the soldered seam.

Fluxing of the parts to be soldered may be performed in various ways: by preliminary immersion in the fluxing medium, and then in the molten solder bath, or by simultaneous fluxing while immersing them in the molten solder, on whose surface a layer of molten flux is deposited.

When soldering parts are soldered in molten solder baths, usually the whole surface of the parts is tinned. In certain instances tinning may be undesirable and therefore, after soldering, the tin layer is to be removed either mechanically or chemically. So, for instance, after soldering bicycle frames with liquid brass solder, excess solder is to be removed from portions of the frame which should not be tinned (this operation is termed de-brassing) thus reducing efficiency of this method, and increasing the consumption of brass and electrical energy /10/.

Another disadvantage of this method is the relatively rapid impurification of the bath by the alloying components of the parts, dissolved in the molten solder during soldering or tinning.

In certain cases, e.g., in baths with low-melting solders of the Sn-Pb system, considerable liquation of the alloying constituents may be noticed, which deprives the upper layers of the bath of its components of large specific weight. Therefore, in using such baths, they should be continuously stirred, the composition of the bath should be thoroughly checked, and if necessary, refining and adjusting of the composition should be done.

Soldering in liquid-solder baths is used largely for uniting copper, copper alloys, and steel parts with low-melting solders. This method is particularly well suited to soldering of such parts as radiators, armatures of electrical machines, and other parts intricate in shape, usually soldered with the POS18, POS40, POS61 and other solders.

Baths for soldering with liquid low-melting solders are usually made of cast iron. As a rule, heating of the bath is achieved externally by means of a nichrome heating-coil placed between the bath and its jacket and covered with a thermal and electrical insulating material.

Before soldering, the parts are to be degreased and pickled.

In order to improve the quality of the soldered work, certain parts are tinned after pickling and rinsing, and then assembled prior to soldering. Hot tinning is also used to prevent corrosion of steel, copper or brass parts.

Degreasing of the parts prior to their tinning or soldering is accomplished in a solution composed of 50 g Na_3PO_4 , 50 g Na_2CO_3 and 1 l water. The degreasing power of the solution may be intensified by adding 10-15 % water glass. Degreasing may be done also in a solution of 20-50 g soda and 1 l water. The degreasing solution is poured into the bath and then preheated up to 50-80°C. Treatment of the parts in the solution of the first composition is completed within 30-40 min, whereas, in the solution of the second composition, treatment is accomplished in 5-10 min.

Pickling of the work is done in wooden or metallic vats, lined with lead sheets and filled with the pickling solution.

The surface of the parts pickled prior to soldering, should not exhibit any traces of scale, residues, precipitated crystals, impurities, or of overpickling.

It should be stressed that iron parts should not be pickled simultaneously with copper or brass parts.

Prior to their immersion in the soldering bath filled with a POS40 solder, the parts to be tinned or soldered are fluxed in an aqueous solution of zinc and ammonium chlorides of the following composition: (by weight) zinc chloride*, 5-7 % ammonium chloride, and the remainder, water; the content of free hydrochloric acid in the flux should not exceed the limits of 0.6-0.8 % (by weight).

The work is to be immersed in the fluxing solution to the required depth. Duration of fluxing is 3-5 min; after fluxing, the work is suspended above the bath for 1-2 min, in order that residues of flux be run off. Oxide films deposited on the surface of the parts to be immersed, are removed by means of a wooden shovel. The surface of the molten solder should have a bright color with a golden or blue-green shade, without crystalline grains or globules. Prior to immersion, the solder is to be heated up to 330-360°C. The parts are kept in the bath filled with a POS40 solder, for about one minute. After soldering, the parts are suspended above the bath for 30 sec, in order that residues of excess solder can run off.

When tinning is carried out in baths filled with a POS18 solder, precautions should be taken to prevent oxidation of the surface of the liquid bath and the parts to be tinned during cooling in open air. For that purpose, the surface of the molten solder before the parts are immersed, should be covered with a layer of ammonium chloride; after 2-3 min, the surface of the bath is cleaned with a wooden shovel. When the parts immersed in the bath are turned around, their surface is covered again with ammonium chloride. The work is then removed from the bath, shaken, and cleaned from residues of molten solder; it is covered again with ammonium chloride, and quickly rubbed with hot oakum to assure a uniform, neat coating. The

* [Translator's note: Russian text gives no percentage.]

tinned surface should be neat, without dark or rusty spots, blisters, bubbles, or scratches.

The work, finally assembled of pretinned parts, is soldered in a liquid-solder bath in the same order: first fluxed in a solution of zinc and ammonium chlorides, and then immersed in the bath filled with molten solder. In order to remove any excess of molten solder from the surface of the soldered parts, they are sometimes charged in a special centrifuge rotating with a speed of 1100 rpm; while rotating, the centrifuge removes any excess solder which is collected in a special container of the unit /17/.

After soldering, the tinned surface of the parts should be smooth without adhesions or flaws of molten solder. When necessary, resoldering should be done without flux, and no later than 10 min after soldering. In resoldering, the temperature of the bath should be kept within 340-360°C.

After soldering, residues of flux left on the soldered parts are removed by rinsing in hot running water heated to a minimum temperature of 70°C. The cleaned parts are dried in a ventilated drying oven (chamber) at 100-120°C.

During tinning and soldering in molten solders, the latter are gradually impurified with copper, iron, zinc, or other metals.

An increased copper content in POS18, POS40 or POS61 solders, leads to an increase in the melting point and viscosity of the solder. A further increase of the soldering temperature should not occur since it would promote dissolution of copper during soldering of the last lot of parts, and cause still greater changes in the composition of the bath.

The increased iron content in the liquid solder due to the deposition of crystalline iron compounds on the tinned surface, lowers the quality of tinning, thus leading to a rough surface of the tinned layer, and sometimes to formation of dark gray spots. Therefore, the chemical composition of the tinning and soldering bath should be systematically controlled. As soon as the copper content surpasses the limit of 0.5%, the bath should be cleaned thoroughly.

An indirect control of the composition of the molten solder may be done by weighing the parts before and after soldering. If the additional weight exceeds the rated value, this means that the composition of the solder underwent certain changes; in such a case a chemical analysis of the molten bath would be necessary.

Iron impurities from baths filled with molten tin or tin-lead solders are removed with coal. For that purpose, minute charcoal is added to the bath, the latter being stirred for 20-30 min. The charcoal, added to the bath carburizes the iron dissolved in the molten solder, forming carbides which may easily be removed by a wooden shovel, since they are floating on the surface of the bath.

In order to reduce dissolution of copper in liquid solder, it may be recommended to add small quantities of antimony /17/. Tin and tin-lead solders are refined by means of sulphur or a mixture of colophonium and charcoal, and by dry, clean saw-dust. Sulphur, colophonium and charcoal are applied in powder form. For full removal of copper from molten solders, sulphur is added to the bath in a quantity of 50-100% of the weight of copper (contained in the bath), mixed with 70% colophonium and charcoal (in proportion of 1:3 of the weight of sulphur). Refining is carried out at a temperature of 240-260°C, in the following manner. Sulphur is added to the bath in small portions for 10-15 min, the bath being continuously stirred with a

mechanical agitator. The mixture of colophonium and charcoal is introduced after the copper sulphides are floating off on the surface of the solder. The bath is then heated up to 320-350°C and held at this temperature for 30 min, while it is steadily stirred. On the surface of the bath a dry black powder is formed which is not wetted by the liquid solder, and may be removed by means of a scraper or a skimmer. After removal of the powder, the bath is covered with a layer of sawdust, at least 3-4 mm thickness, which is fired in several places. After burning of the sawdust, the refining process is believed to be completed. Subsequent chemical analysis of the solder helps in checking the quality of refining.

As a result of differences in the specific gravities of lead and tin in tin-lead molten solders, liquation phenomena may be noticed: the upper layers of the bath are richer in tin, the lower, in lead. The parts immersed in the bath usually are soldered and tinned in the upper layers; consequently, the average composition of the solder will be poor in tin and rich in lead. This may cause a certain roughness of the tinned surface of the parts due to excess lead-crystals precipitated on the tinned surface.

In order to adjust the composition of the bath, once in 24 hours a chemical analysis of the molten solder after its thorough stirring should be carried out to check the tin content; alternately, the tin content may be determined according to the specific weight of the solder, which may be computed for Sn-Pb alloys with 20-60 % Sn by the following formula:

$$C_{\text{Sn}} = \frac{10,26 - \rho}{0,044} + 20,$$

where C_{Sn} = tin content in parts per weight; ρ = specific gravity of the alloy /18/.

If necessary, a definite amount of tin may be added to the bath to make up for losses.

In the course of operation, the bath with molten flux may become impurified with mechanical or chemical foreign matters (copper compounds). Cleaning the fluxing baths from mechanical impurities is done by filtrating through glass wool; the dissolved copper compounds (which impart a blue color to the solution) are extracted from the bath by pickling in a fluxing solution of ground metallic zinc; in this solution copper is precipitated in the presence of free hydrochloric acid.

During bath soldering with low-melting solders, residues of flux or oxide films are often found on the soldered seam. In certain cases, on the soldered parts traces of frozen solder beads may be noticed. Such defects are particularly undesirable in soldering printed circuits, since they may disturb the order of connecting the electrical contacts to the conductors of the printed circuit. The so-called spray soldering method (a variety of dip-soldering) is free of such defects.

In this method, soldering occurs when the parts to be soldered come into touch with the molten solder sprayed on the surface of the liquid bath. The solder jet is formed when molten solder is fed through a long narrow nozzle immersed in the bath, (Fig 83). The jet of molten solder, while touching the soldered seam, removes the flux; this method improves the heating conditions of the soldered seam, the surface of the solder being thereby cleaner and free of oxides or other impurities; it prevents also

formation of false seams, and assures a rigid bond of the finally soldered seam.

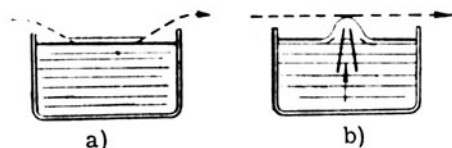


Figure 83. Diagram of the method of vertical immersing (a), and of spray-soldering (b) of the parts to be joined

In order to prevent gathering of frozen solder droplets on the soldered parts, they are shaken slightly during soldering.

The height of the solder jet over the surface of the bath may easily be controlled by means of the solder feed pump. When using the spray soldering process, the printed circuit is to be moved with a certain speed (0.7-1.2 m/min) over the surface of the bath. The waste of molten solder, connected with this method, may be compensated for by gradually immersing the soldering stick into the soldering bath, using a special floating regulator. Thanks to the pumping of the molten solder through the nozzle, the molten solder is continuously stirred [19/, /20/.

Soldering of printed circuits may be done also by the method of preferential soldering combined with forced feed of the molten solder through a special die (this method has been devised by V. F. Minkov). In this method, the printed circuit is placed on the die and fastened to it by special jigs. This prevents warping of the circuit and swelling of the conductors, and it protects the current-carrying parts from action of the liquid solder.

In order to ensure both a thorough flowing of the molten solder into the openings of the printed circuit, and good gathering of the molten solder into droplets, 2-3 sec after immersion of the circuit (50-70 % of its thickness), the vibrating device (frequency of oscillations 100 c/s, amplitude 0.1-0.3 mm) should be switched on.

Soldering of printed circuits at a temperature of 170-190°C requires a special flux prepared from a mixture of 30 % stearin and 70 % paraffin; the effectiveness of the latter is slightly higher than of a colophonium-alcohol flux. The stearin-paraffin flux has some insulating properties and is used together with the POS61 solder without subsequent removal of the residues by rinsing.

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Chapter X

FURNACE SOLDERING

Though furnace heating of metals and alloys prior to soldering has been known for a long time, it was the invention of the electric furnace, and its growing industrial use that broadened the scope of this soldering method (which made direct application of this method possible). Direct-heated combustion-furnaces do not permit fine adjustment of temperature, and therefore, are seldom used in soldering operations. On the other hand, in electric furnaces temperature may be easily controlled, thus permitting mechanization of the soldering process.

Parts soldered in electrical furnaces are less subjected to warping than in welding, or in soldering by local heating; electrical heating improves homogeneity of the soldered seam, and reduces discrepancies in the mechanical properties of the soldered joint /1/. For soldering temperatures up to 1100°C, furnaces fitted with nichrome heating elements (resistors) are used. Heating of the parts to a soldering temperature up to 1300°C, may be done conveniently in furnaces with selite or carborundum resistors*. In certain instances, high-temperature electric furnaces with molybdenum heating elements assure a heating temperature above 1200°C. Side-opening furnaces are less employed.

The flux-covered furnace-soldering method is most commonly used. Flux soldering may be suitable in cases where other methods of oxide removal from the solder and soldered parts have proved to be ineffective. At present fluxless methods of furnace soldering (see Chapter XV), soldering in atmosphere-type furnaces (with reducing or inert gases) and vacuum soldering methods are largely employed.

Furnace soldering of metals and alloys under a flux layer, is used in cases where oxide removal from the soldered surface is impossible by other methods.

Use of an inert or reducing-gas atmosphere for soldering of steel, copper, nickel, or other metals and alloys, involves provision of additional equipment. Therefore, in small-scale production such metals are soldered by the flux soldering process.

Soldering of certain steel parts intricate in shape, in which removal of flux residues is often very difficult or quite impossible, may be performed

* For instance, G-50 type furnaces for heating of large-sized parts, G-30 type furnaces for heating of smaller parts, OKB-210, OKB-333 furnaces etc.

with gaseous fluxes such as hydrogen fluoride, ammonium fluoride, ammonium fluoborate, or boron fluoride /2/.

§ 1. Preparation of the Work for Furnace Soldering

Preparations of the parts before their furnace soldering covers the following stages: preparation of the surface to be soldered, assembling and fastening of the parts, and proper placing of the solder and the flux.

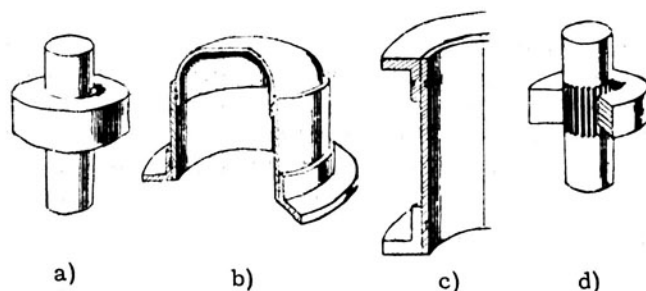


Figure 84. Some methods of fastening prior to soldering:
a—punching; b—tack welding; c—pin fastening; d—knurling.

The parts to be soldered are fastened to special supports made of refractory brick, graphite, heat-resistant alloys, or of other adequate materials. The assembled parts are fastened by different methods /3/.

To prevent shifting of the parts during soldering, the punching method of fastening is sometimes used.

Parts to be soldered subjected during soldering to stresses or loads, may be fastened by a drive, press, or close running fit. Drive fit is often used in copper soldering. It should be stressed, that a fast tightened press fit may sometimes lead to inadmissible distortions of the parts as a result of their expansion upon heating above the elastic limit, which in turn may cause cracking and weakening of the soldered seam. In socket-type couplings (muff-couplings), a loose or tight fit may be achieved if one of the joined parts has a straight notch /4/, /5/.

Parts of high mechanical strength are fastened by knurling with subsequent pressing, by grooving, mandrel expanding, knurling, tack welding, and screwing (Figure 84). Mandrel expanding is useful in pressing tubular parts into a nozzle. In expanding, contact of the parts on a single line only should be avoided. For that purpose, before expanding, a mandrel is inserted into the tube, which supports the wall of the tube during expanding.

In soldering cutting tools (e.g. milling cutter), frequently the method of wedging is used which consists of pressing into special grooves, heat-resistant steel, mica, or porcelain pins or wedges, which assist in maintaining the constant position of the parts during soldering (Figure 85).

Wedges of non-metallic materials prevent welding of the hard-alloy

lamellae to the opposite wall of the part. Upon cooling, such welding may lead to cracks /7/. In the manufacture of tubes with external fins, for a more intense heat transfer, the fins are wound on the tube wall with their narrow edge. Copper-wire solder is then placed along the fins.

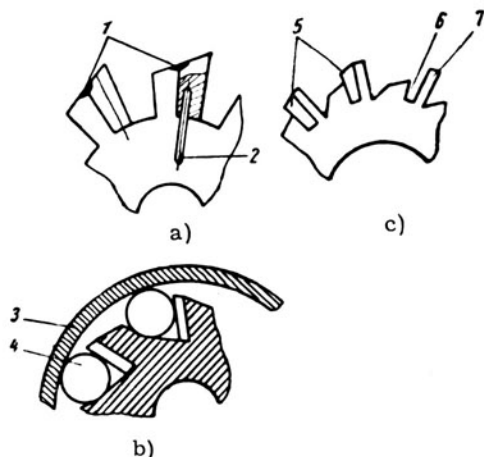


Figure 85. Other methods of fastening before soldering:

- a—by pins and tack welding; b—by a bandage and small carbon cylinders;
- c—fastening by means of an elastic wall: 1—tack welding; 2—pin;
- 3—asbestos cord; 4—carbon cylinders; 5—hard alloy; 6—groove for hard alloy lamella; 7—fastening wall.

For soldering parts of cash-registers, the work is fastened by tapered pins driven in the shaft which supports the parts to be joined.

In soldering of hollow parts with a precise bore (e.g. bushings with a handle), the method of spinning on a riveting machine, or unriveting on a press is employed; this involves a preliminary reaming of the bore. To assure a close gap (clearance) between the parts to be soldered, e.g. in lap-soldering of bulky parts, often the method of hammer peening is applied. This proves to be satisfactory in instances of a complicated lap joint (see Figure 3).

Usually as a result of deformations during soldering, lengthy lap-joints exhibit local swellings and leakages. For this reason, such types of joints, which do not lead to uncovering of the seam during furnace heating, are more suitable (see Figures 6, 9, 10, 11). In these types of lap-joints, particular attention should be paid to proper placing of the solder, in order to insure thorough penetration of the molten solder into the gap. For fastening, the spot welding method is more convenient. In order to assure a correct position of the parts during soldering, supports and holdings are sometimes used, but only if absolutely necessary, since they involve prolonged heating, which increases the duration of holding in the furnace, and reduces the efficiency of the process. Metallic supports and holders are liable to be subjected to corrosion; it has been found more satisfactory to make them of graphite or alundum covered with a thin asbestos layer to prevent carburizing of the parts to be soldered.

If fastening of parts is done in special jiggging appliances, the jigs are to be made of heat-resistant steel or alloys; the thread should have a loose fit to facilitate unscrewing of the nuts after soldering.

Band or wire supports may be more conveniently made of nichrome (80 % Ni and 20 % Cr). All the metallic appliances should be covered with a thin asbestos layer, or with an oxide coating, to prevent soldering the appliance to the work.

For high-temperature furnace-soldering the parts are sometimes fastened by means of a pneumatic cushion. For this to be done, the work is placed in a container, where a pneumatic cushion has previously been inserted between the wall and the work; in soldering, compressed air or nitrogen is fed into the cushion under a pressure of $2-5 \text{ kg/cm}^2$, thus assuring tight fastening of the part.

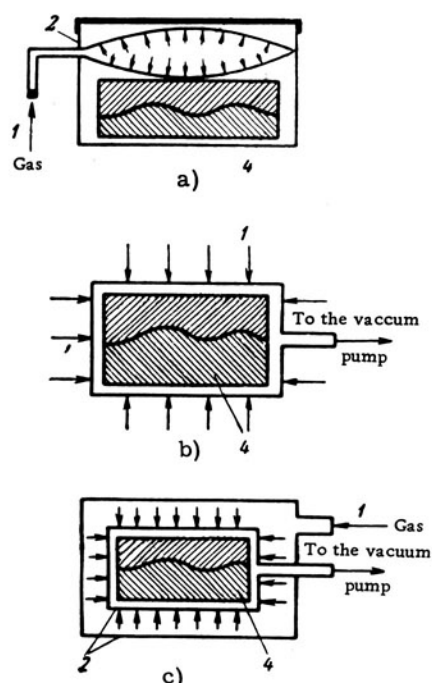


Figure 86. Methods of clamping the parts to be soldered:

a—by a pneumatic cushion: 1—pressure fed gas; 2—container; 3—pneumatic cushion; 4—the part to be soldered; b—clamping due to the pressure difference between the outer and inner walls of the container; c—combination of the first two methods

The pneumatic cushion is made of low-carbon or stainless steel sheets (sheet thickness, 0.7-1.0 mm) in the following manner. Two pieces of sheet, of the same size, are placed one above the other, and then the edges are seam-welded. Due to the pressure of the gas fed into the cushion through a special tube, the parts are clamped by the cushion to the walls of the container (Figure 86, a).

Pneumatic clamping may be achieved in the following manner: the parts to be soldered are placed in a thin-walled steel container, similar in shape to the parts. After pumping out the air, the parts are clamped to the walls of the container, due to the pressure difference between the outer and inner walls (Figure 86, b). The clamping container may differ in shape from the parts to be joined. In such cases, it should be filled with a heat-resistant material, e.g. thermocorundum, through which the pressure is transmitted from the walls to the parts to be soldered. The pressure exercised on the walls, may be increased by inserting the container in a thick-walled vessel (e.g. of tubular shape), through which gas is pressure fed (Figure 86, c).

In certain cases, when soldering large-sized parts, clamping is achieved in special dies closely encircling the assembled work, and heated in furnaces or by an external heating coil.

In furnace soldering, common practice is to place ring or wire-shaped solder around the seam or on some projections of the work, near the seam. Sometimes the solder is placed in special grooves; to compensate for the heat expansion of the wire or ring-shaped solder during heating, which is liable to cause warping of the solder, the latter is to be placed in separate pieces (maximum length, 150 mm) one above the other. If in the course of assembling, the solder is placed inside the gap, it may have any length and shape /6/. The solder should be fixed to prevent it from shifting when charged into the soldering furnace.

§ 2. Equipment for Flux-Covered Furnace-Soldering

For soldering, horizontal or low-shaft electric furnaces may be employed. Care should be taken that the temperature gradient in the space of the furnace occupied by the work to be soldered, be within the limits of the working soldering range. Control of furnace-soldering should be done with a well adjusted and calibrated thermoregulating device. In order to protect the heating elements from the action of liquid flux, preference should be given to electric furnaces with ceramic full-muffles. The furnace should be provided with a fume exhaust system.

The technological equipment for furnace soldering, usually comprises bottom plates and fixtures preventing shifting of the parts during soldering, sagging under their own weight, warping, etc.

This sort of equipment is made of heat-resistant steel (of the chrome or chrome-nickel grade). Care should be exercised, that the coefficients of thermal expansion of both equipment and the parts to be soldered, be the same or nearly the same, otherwise the parts will shift during soldering.

Bottom plates are required for handling and transporting the parts in the process of soldering. For easier handling, the bottom plates are often provided with special dowel pins on which the items are placed. The requirements which the bottom plates have to meet, generally consist of the following: assurance of uniform heating of the work, prevention of shifting throughout the soldering process.

§ 3. Flux-Covered Furnace Soldering

The work ready assembled for soldering is charged into the soldering furnace heated to the requisite soldering temperature. The heating time of the work depends on the thickness of its seam area, on the size and volume of the fixture (appliance); it is determined for each job largely by experiment. The time of keeping in the furnace is measured from the moment when the furnace reaches the soldering temperature.

Furnace soldering of aluminum has its peculiarities. It is of extreme importance to assure an accurate control of the temperature inside the furnace where the work is placed for soldering. For most alloys, the working soldering range does not exceed 10-30°C being for many alloys near the solidus line; this may lead to overheating and burning of the work. Therefore, in soldering aluminum and its alloys, the temperature of the work should be checked by means of a thermocouple fixed on the edges of the parts along the furnace. If for certain reasons the required temperature gradient cannot be achieved and a part of the work is heated below the soldering temperature, heating may be done in two stages, rotating the work so that the unsoldered part, during subsequent heating, may reach the requisite soldering temperature.

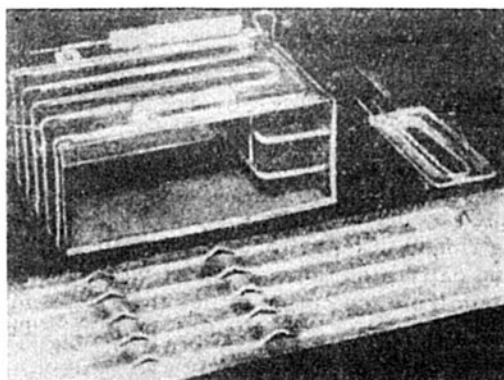


Figure 87. Furnace-soldered aluminum evaporator

Burning or fusing of the part to be soldered, may be prevented by using ventilators for levelling the air temperature in the furnace as well as containers or asbestos sheets blanketing the work from direct contact with the flame.

The 34A flux, usually required for soldering aluminum items, dissolves not only the oxide film but the base metal too. In soldering thin-walled, and particularly foil-shaped parts, this sort of flux should be applied only after the work is heated in the furnace up to the melting temperature of the solder. When the flux is added during assembling, heating of the work up to the soldering temperature should be done quickly (5-15 min) to reduce the time of interaction between the liquid flux and the base metal, and to prevent corrosion of its surface.

Figure 87 shows furnace soldered aluminum radiators. Furnace soldering may be applied also to copper, structural, stainless, heat-resistant or acid-resistant steel parts, using the required soldering and fluxing materials, and taking the same precautions as for aluminum soldering, i. e., rapid heating of the parts, keeping a constant heat-gradient along the work within the rated soldering range, and thorough clamping of the parts to be soldered.

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Chapter XI

SOLDERING BY SOLDERING LAMPS OR GASEOUS TORCHES

In soldering thick-walled or large-sized parts with low-melting solders, or conversely in soldering small parts with high-melting solders, the usual soldering bit may prove to be insufficient to afford the necessary heat. In such cases this heating method may be replaced by local heating, the heat being generated in a special appliance, in which a mixture of air or oxygen and liquid or gaseous fuel is burnt. Liquid fuels are kerosene, gasoline, alcohol, etc; gaseous fuels are acetylene, town gas, buthane, propane, etc.

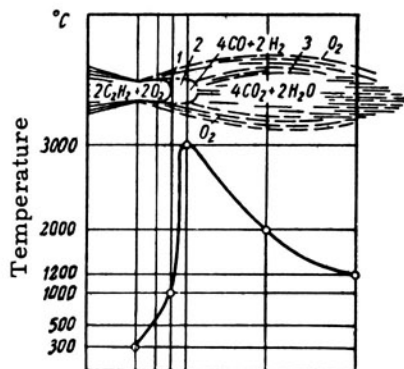


Figure 88. Structure and temperature of the oxy-acetylene flame:

- 1—inner tip (the cone); 2—central zone of the flame (called the beard or brush); 3—the outer (non-luminous) envelope.

The flame generated by burning these fuels, represents burning incandescent vapors and gases. Brightness of the flame depends on the presence of incandescent solid particles; in the absence of such particles (e. g. in a hydrogen or alcohol flame) the flame has a non-luminous and pale appearance.

The flame of a burning fuel mixture usually has three zones of combustion: the inner cone (tip), the central zone termed the beard or brush,

and the outer envelope (the flame proper). Figure 88 illustrates schematically the structure of an oxy-acetylene flame. Shape, sizes and temperature of the zones of the flame vary and depend on the concentration of oxygen in the combustible mixture, on the speed of delivery, and of the composition of the fuel employed.

The fuel gases or vapors are fed to the combustion appliance (burner, torch, etc.) under pressure. The air or oxygen, necessary for combustion, may be obtained directly from the surrounding medium or under compression. The air from the atmosphere is picked up by the combustible gases when leaving the nozzle; oxygen is usually fed under pressure from special bottles. The principle of air-intake from the environment is applied also in soldering lamps.

§ 1. Soldering by Soldering Lamps

Soldering of small sized items with relatively low-melting solders, is done by soldering lamps. Soldering lamps use chiefly liquid fuel (kerosene, gasoline, or alcohol) or liquefied petroleum (oil) gases (butane, propane, etc).

A soldering lamp has the following construction. From the fuel container (reservoir) the fuel, under a definite pressure is drawn (sometimes through a wick) into the vaporizer where it changes from the liquid to the gaseous condition. The combustible gas then mixes with the absorbed air forming a combustible mixture which burns upon its discharge from the nozzle outlet. The amount of combustible gas delivered may be controlled. Below the vaporizer, a trough is provided to hold a small quantity of alcohol or gasoline for heating up the vaporizer when starting the torch.

Delivering the liquid fuel through a wick from the reservoir to the vaporizer is very slow, and therefore lighting the lamp (at a low temperature of the surrounding air) is quite a difficult task. At present this type of lamp is gradually being replaced by soldering lamps provided with a pump for delivering the liquid fuel under pressure from the reservoir to the vaporizer.

Working with a soldering lamp is linked with the danger of explosions. Therefore, in handling such tools, certain precautions should be taken; these refer particularly to interdiction of the use of alcohol, or gasoline for washing the torch and filling of the reservoir with liquid fuel; working only with the rated sort of liquid fuel; provision of air holes in the cover of the reservoir (for ventilation).

Certain designs of soldering lamps allow change of the burning nozzle when the sort of fuel is changed.

Many data about improvements and additional features in design and construction of soldering lamps, may be found in the literature (periodicals and patent descriptions), which ensure increased stability in working and use of cheaper liquid fuel /1/.

Upon prolonged use, soldering lamps are usually overheated. From time to time they should be switched off in order to be cooled. The soldering lamp of improved design possesses an additional water-filled jacket in which the fuel reservoir is placed. Such a design prevents overheating of the lamp even after prolonged (8-hour) operation /2/. Figure 89 presents construction of such a soldering torch.

Common soldering lamps have an essential disadvantage: the helical tube of the vaporizer tends to clog. Since mechanical cleaning of the tube with its peculiar shape is impossible, one resorts to burning, or gas pressure cleaning, which does not always have the desired effect. In soldering lamps with straight channel burners and fuel feeding tubes, the latter are easily cleaned by means of a piece of wire, after loosening the screws in the channels /3/.

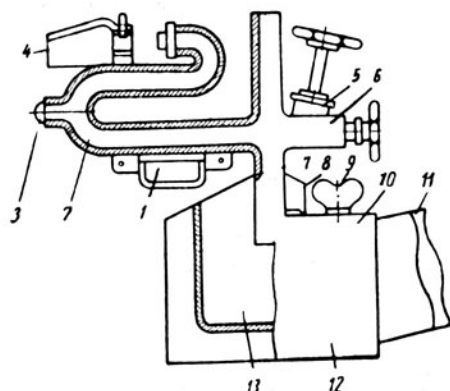


Figure 89. Modern design of a water-cooled soldering lamp:

- 1—trough for preheating of the fuel; 2—L-shaped burner pipe; 3—cleaning hole; 4—cone cylinder of the nozzle; 5—delivery pump; 6—three-hole piece; 7—connections of the burner with the reservoir; 8—opening for filling of water; 9—openings for filling of fuel; 10—cooling jacket; 11—handle; 12—water outlet; 13—fuel reservoir

Soldering of parts heated by the soldering lamp occurs in the following manner. The seam area is covered with a flux layer and heated until the soldering rod, fed to the seam, starts to melt. Soldering takes place with a continuous delivery of solder and flux to the seam area.

In soldering aluminum alloys with high-melting solders using the 34A fluxing agent, the soldering technique is slightly different. After prolonged contact with the torch flame, the 34A flux loses its effectiveness. Therefore at first, the parts and the solder are to be preheated to 300-400°C, and then the solder rod, previously soaked in dry flux is rapidly passed over the work along the seam, without stopping to heat the work.

Heating of the work should be interrupted when the molten solder, touching the parts on the seam area has filled the gap and formed a convex bead on the opposite side of the joint. Care should be taken that, during heating, the solder should not be molten while still in the rod, but only after touching the work on the seam, since otherwise, the solder fails to fill in. the gap in places not sufficiently preheated. After formation of convex bead, the soldered seam should not be reheated in order to improve appearance of the joint, since this may lead to over-heating of the base metal, and to appearance of porosity in the seam.

After soldering with the lamp, any traces of flux should be thoroughly removed.

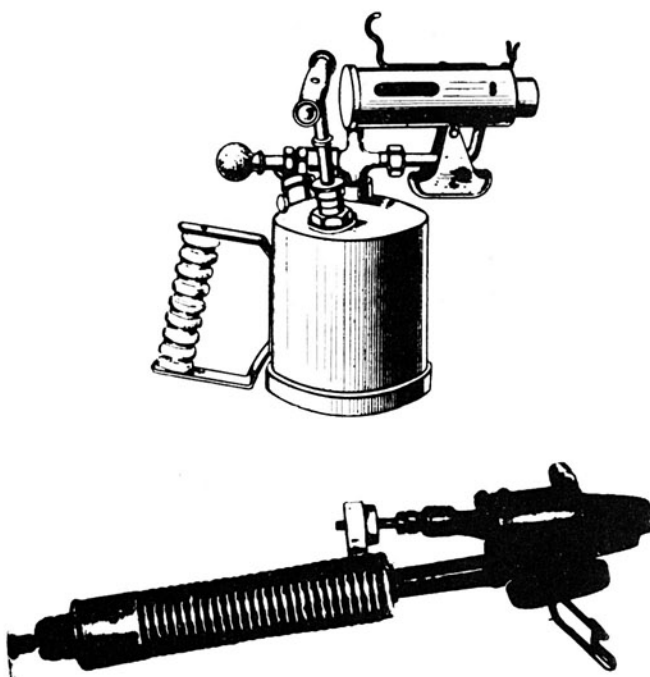


Figure 90. General view of gasoline soldering lamps

Preheating of the soldering lamp is applied in soldering parts of different metals and alloys. In soldering aluminum and its alloys with high-melting solders and 34A fluxes, heating by the oxy-acetylene torch should be avoided, and preference should be given to the gasoline soldering lamp (Figure 90).

§ 2. Soldering Blow-Pipes

For soldering small parts in jewelry and denture work, a blow pipe is commonly used. The temperature of the flame is increased by blowing an air jet through the pipe. In such cases, the flame is generated by burning oil, alcohol, etc /1/, /4/.

As said, the air is blown in by means of a blow pipe. Since working with the blow pipe is tiresome, the operator uses a rubber ball to blow in the air.

When working with a blow pipe, the combustion air may be delivered also from a pneumatic unit, usually employed for driving pneumatic tools. Further development of the mouth blow-pipe lead to the present-day soldering gas burners. The existing patents in this field chiefly deal with methods of controlling the gas and air delivery.

§ 3. Use of Soldering and Welding Torches

Rapid heating of the parts to be soldered to relatively elevated temperatures (above 600°C) may be done in gas torches in which a combustible mixture of air or oxygen and different combustible gases or vapors is brought to combustion.

Table 75 presents some data on the flame temperature for certain combustible substances /5/.

Table 75

Flame temperature of certain gaseous fuels

Gaseous fuel	Approximate temperature of the gas-oxygen flame, °C	Air or oxygen content in the combustible mixture, leading to deflagration, %	
		Oxygen	Air
Acetylene (C ₂ H ₂)	3150	2.8-93.0	2.2-81.0
Hydrogen (H ₂)	2100	2.6-93.9	3.3-81.5
Methane (CH ₄)	2000	5.4-59.2	4.8-16.7
Ethane (C ₂ H ₆)	2050	4.1-50.5	3.1-15.0
Propane (C ₃ H ₈)	2050	-	2.2-9.5
Butane (C ₄ H ₁₀)	2050	-	1.5-8.4
Town gas (Moscow type)	2000	10.0-73.6	3.8-24.8
Kerosene vapors	2300	-	1.4-5.5

The oxy-acetylene flame has the highest temperature and therefore in gas welding of metals it is largely used for fusing the edges of the parts to be joined.

Since during soldering the edges of the parts to be soldered are heated only to the melting point of the solder, the necessity of intense heating no longer exists. Moreover, too intense heating is even undesirable as it may lead to a local overheating of the base metal. In this connection, oxygen may be replaced by air, and acetylene by gaseous fuel.

When oxy-acetylene torches are used for soldering purposes, heating is done by the outer cooler zone of the flame (envelope), in which the temperature does not exceed 2000-2500°C.

An excess of oxygen in the combustible mixture produces an oxidizing flame, an excess of combustible gas produces a reducing flame. To obtain a normal flame, gaseous fuel and oxygen should be mixed in a definite proportion, varying with the fuel gas.

So, for instance, the proportion of acetylene to oxygen in a combustible mixture (Figure 91) may be computed by the formula

$$\beta = \frac{O_2}{C_2H_2} = 1.1-1.2$$

The inner cone of this flame has a sharply designed contour. At an

excess of oxygen ($\beta > 1.1-1.2$), the inner cone of the flame becomes shorter and cone-shaped; at an excess of acetylene, the inner cone becomes longer and coincides with the envelope; presently it may have no central zone (beard) at all.

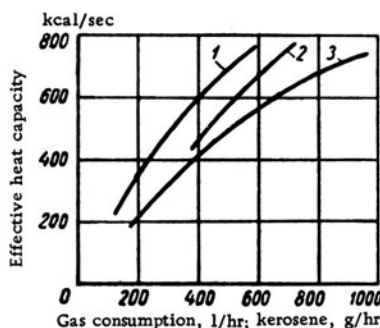


Figure 91. Chart for computing the equivalent consumption of gaseous fuel, as substitute for acetylene:

1—acetylene, $\beta = 1.15$; 2—kerosene, $\beta = 2$; 3—town gas, $\beta = 1.3$

The amount of heat furnished to the work in a time unit (efficiency of flame) depends on the fuel consumption; by proper control of the consumption of gaseous fuel (substituted for acetylene), the same efficiency as in an acetylene flame may be obtained.

The coefficient for replacing acetylene by other gaseous fuel, may be found as follows:

$$\psi = \frac{V_s}{V_a}$$

where V_s = consumption of the substitute gas, V_a = consumption of acetylene.

In the following some coefficients for different gaseous fuel are given: methane $\psi = 1.7$; coke oven gas, $\psi = 3.2$; town gas (Moscow type), $\psi = 2$; kerosene vapors, $\psi = 1.35$. These gases, when used instead of acetylene, do not alter the rate of soldering, and the quality of the soldered joint.

Gas soldering with high-melting solders is usually done with an oxy-acetylene welding torch. The VNII Avtogen [Vsesoyuznyi nauchno-issledovatel'skii institut Avtogen (All-Union Scientific Research Institute of Auto-genous Welding)], devised special torches for soldering both with acetylene, and with a substitute. Such a soldering torch is actually a usual injector welding-torch, provided with an expanding tip through which the flame is ignited.

The common SU-type injector welding-torch for burning an oxy-acetylene mixture, is fitted with multi-flame tips assuring a softer flame and a more uniform heating, both necessary in soldering large-sized parts with long seams /5/.

If using town gas (of the Moscow type), the common SU oxy-acetylene torch with special NP-C nozzles, may be used /6/. These nozzles differ from the usual by the sizes of the openings in the tips, injectors, and mixing devices. NZP-type nozzles are suitable for methane, coke oven gas, and other substitutes for acetylene.

In certain cases, soldering of parts having a wall thickness of 2-9 mm, may be done with oxy-kerosene vapor torches of the GK-52 type provided with two interchangeable tips, No 3 and 4.

Characteristics of the GK-52 oxy-kerosene torch are given in Table 76.

Table 76

Characteristics of the GK-52 oxy-kerosene soldering torch

Characteristics	Thickness of the soldered part, in mm	
	2-6	2-9
No of tip	3	4
Pressure in kg/cm ² of:		
oxygen	3-5	5-7
kerosene vapors	1.5-2.5	2.5-3.0
Consumption of:		
oxygen, l/hr	540-820	820-1100
kerosene, g/hr	390-550	550-720

In soldering with gas torches and soldering lamps, the solder is usually fed to the seam by hand. Use of granular, foil, or clad solder is limited. The method of introducing the flux is essential in heating with gas torches. The simplest method of introducing the flux, which consists in dipping the previously heated soldering rod in dry flux and transferring it to the seam, may sometimes prove to be unsuitable in soldering with gas torches. Heating of uncoated metals prior to soldering is liable to cause a considerable oxidation of the surface. As a rule, in such instances flux is applied on the seam prior to heating, to develop an oxidation-resistant film. Paste flux may be applied by means of a brush. Sometimes, the parts to be soldered are partially or completely dipped in an aqueous or alcoholic solution of flux.

To assure good wetting of the base metal, the fluxing solution is sometimes preheated to 90-100°C. Apart from this, in soldering, a certain amount of flux is applied together with the soldering rod, by immersing the latter, from time to time, with its hot end in dry flux.

Heating is carried out quickly, so that evaporation of the solvent (water or alcohol) takes place only during melting of the fluxing substance /7/.

Gas torches are used in soldering structural and low carbon steels, copper parts, lead, copper or nickel, alloys /8/-/10/, e.g. in the manufacture of filters for pipe-lines and their fittings, bicycle frames, equipment for chemical and food industry, etc /7/, /11/, /12/.

For gas-flame soldering of aluminum and its alloys, a combustible mixture of oxygen and hydrogen, butane, or propane is employed. Heating is done with a neutral flame. If soldering is done with a more high-melting flux than the 34A fluxing agent, the oxy-acetylene soldering torch, due to the greater stability of its flame, may be used. In such cases, travel of

burner and solder should be done according to the scheme shown in Figure 92, so that the flux melts prior to melting of the solder /13/.

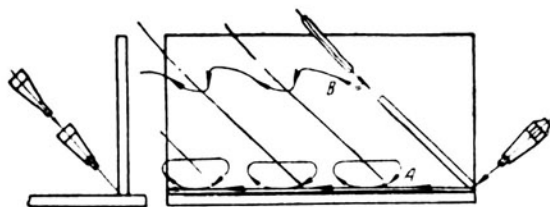


Figure 92. Diagrammatic representation of the travel of the soldering burner (A) and the soldering rod (B) during soldering:

1, 2, 3—points of contact between the solder and the base metal

Recently, special gaseous fluxes have been devised which are delivered to the combustible mixture from a flux feeder mounted between the gas bottle and the burner.

Such gaseous fluxes are methylborates dissolved in methyl alcohol together with acetones (e.g. the BM-1 flux). The Institute of Autogenous Welding devised a special flux-feeder of the FGF-1 type, connected to a common oxy-acetylene torch.

Gaseous fluxes are used in soldering copper, brass, or carbon steel parts. They are unsuitable for soldering stainless steel, for silver-soldering or for soldering of aluminum, magnesium or high-chromium alloys.

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Chapter XII

ELECTRICAL SOLDERING METHODS

§ 1. Induction Heating for Soldering

High-frequency induction heating is one of the most efficient methods of heating, used largely in heat treatment of steel parts, melting of alloys, and soldering as well /1/-/4/.

The main advantage of this method as compared with flame heating or heating in conventional electric furnaces is rapidity, which reduces the possibility of oxidation of the surface of the parts to be soldered. Rapid heating also prevents an intense growth of the crystalline grain as well as the development of recrystallization phenomena in the soldered joint. This method also permits local heating of the parts to be soldered.

In the high-frequency induction method, metallic parts, if placed in a circuit, are heated due to an intense electromagnetic field (eddy currents) produced when a strong alternative current flows through this circuit.

The intensity of the induced current is given by

$$I = \frac{E}{Z} = \frac{4.44 f \omega \Phi \cdot 10^{-8}}{Z} a.$$

where Z = apparent impedance of the circuit, in ohm; E = electromotive force, in v; f = frequency of current, in c/s; ω = number of loops (turns) of the heating circuit; Φ = magnitude of the magnetic flux.

The current induced in the conductor flows in an opposite direction to that of the current passing through the loop. As shown by the formula given above, the magnitude of the current passing through the conductor is proportional to the frequency of the alternative current flowing through the loop, to the number of the loops, and to the magnetic field /5/.

The density of the induced current (like any alternating current) varies throughout the cross-section of the conductor, and is determined by the magnitude of the electromagnetic and magnetic fields of the closely placed conductors. In conductors through which alternating current is flowing, as a result of interaction of the magnetic fields three effects may occur: the skin, the proximity and the coil (annular) effects. They should be taken into account when heating metals by the induction method. Non-uniform current density in the cross-section of the conductor, due to these effects, may lead to a non-uniform heating of the conductor (Figure 93).

The skin effect results from the fact that density of an alternating current passing through a conductor, has a maximum value on the surface of the conductor, and decreases from the surface to the center line.

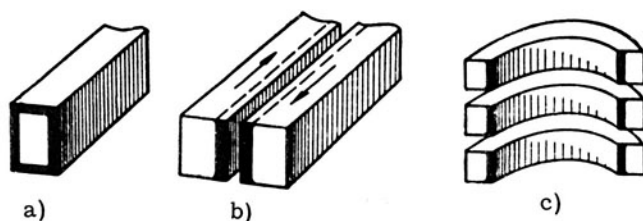


Figure 93. Diagrammatic representation of the action of the skin, proximity, and coil effects:
 a-skin effect; b-proximity effect; c-coil effect.
 Dark places indicate concentrations of magnetic lines of force

The higher the frequency of the current flowing in the conductor and the greater its conductivity and magnetic permeability, the stronger is the skin effect.

The proximity effect appears as a result of the non-uniform distribution of the current density in the cross-section of adjacent conductors, the distribution depending on the direction of current in those conductors; with the same direction, maximum density of the alternating current may be noticed in the opposite ends of the conductors; for different directions, maximum density occurs on the close ends. If alternating current flowing through closely placed conductors differs in direction, the direction of magnetic lines of force in the field between the conductors coincides; this leads to an increase in the magnetic density of the field.

The above means that the smaller the distance between the conductors, the stronger is the proximity effect.

The coil effect is caused by asymmetry of the electromagnetic field in the conductor rolled up to a coil: the magnetic flux concentrates at the inner surface of the coil and spreads in the outer one.

The higher the frequency of the alternating current, the more intense are the effects discussed previously.

Simultaneous occurrence of these effects may result in strengthening or weakening of their action. So, for instance, if a cylindrical tube is heated externally the coil effect of the inductor coil is strengthened by the proximity effect generated between the inductor coil and the tube walls through which eddy currents flow. Since the current in both the inductor coil and the tube differs in direction, maximum current density and hence, greater heat will be created in the external surface of the tube. By placing the inductor coil inside the cylindrical tube, the heat intensity drops, since in this instance, the coil effect reduces the combined action of both the skin and proximity effects.

The magnitude of the induced current depends not only on the frequency of the applied alternating field, but also on the resistivity of the conductor and its magnetic permeability, both of which are determined by temperature and heating time. Therefore, if applying the induction-heating method, the

character of the heating changes with the variation in temperature. When heating steel parts, their electric resistivity increases with the increase in temperature, whereas the magnetic permeability remains quite unchanged, dropping suddenly only when close to the Curie point (at 800°C). Therefore, during heating of steel a marked skin effect is noticed until appearance of the critical temperature (800°C) on the steel surface. In the affected layer, the skin effect, due to the very low resistivity and magnetic permeability is less significant. Starting from the layer with critical temperature, the heat propagates throughout the work. At a sufficient extension of this layer, the relative amount of heat penetrating into deeper layers decreases, and due to the increasing resistivity of steel, all the energy of the field in this layer changes to heat energy.

When heating paramagnetic metals (copper, aluminum, brass, bronze, etc) the rise of resistivity during heating leads to a more uniform distribution of the induced current, and hence, of the heat.

In induction heating of metals, frequency may vary within large limits: from 50 to $2 \cdot 10^5 - 10^6$ c/s. Soldering usually requires radio-frequency generated by spark or valve oscillators. For soldering large-sized parts with a frequency of 8000 c/s, sometimes mechanical generators are used. This frequency permits a slow and uniform heating thanks to heat conduction and to levelling (equalizing) of the temperature between the outer and inner layers of the work /6/.

In induction heating, the surface of the parts are heated first; heating of the seam area due to heat transfer by conduction occurs slower. Oscillators of more than 30 kva are not recommended for soldering purposes since, prior to melting of the solder, they may cause superficial fusing of the parts, due to heat conduction.

For induction soldering most frequently used are melt-quench type high-frequency oscillators with an output of 10-60 kva and a working frequency of 200-600 kc/s (Table 77).

Table 77

Type of oscillator	Rated output kva	Working frequency kc/s	Dimensions of the unit, mm
LGZ-10	10	600-700	1180 × 1020 × 2030
LGZ-30	30	200-250	1400 × 2300 × 2300
LGPZ-30	30	200-250	2680 × 3680 × 2300
LGZ-60	60	200-250	1400 × 2800 × 2300
LGPZ-60	60	200-250	2680 × 3750 × 2300

Soldering of hard-alloy tips (on cutting tools) is done by means of the VNII-MSS oscillator of 6 kva, 200-250 kc/s; the unit has the following dimensions: size of the base, 1.5 × 0.8 m; height, 2.0 m /7/.

The alternating electromagnetic field round the work to be soldered is generated by the high-frequency alternating current flowing through the inductor coil. Shape and size of the inductor coil are selected to suit the shape of the seam and the dimensions of the parts to be joined. Usually, inductor coils are made of cylindrical or square copper tubes, cooled by a stream of cold water running through the coil. Irregularly shaped inductor coils sometimes are assembled of tubings, rods, or sheets.

Inductor coils are of the detached or permanent-type, having single or multiple loops for heating the work both on the inner and outer side. Quality of soldering, to a great extent, depends on the proper choice of the inductor coil. Since existing methods for the design of inductor coils are mostly empirical, shape of the inductor coil is selected according to practical considerations, being finally adjusted in the course of construction /5/.

The direction of the heating current in the inductor coil should be parallel with the plane of the seam, since an intense current, if flowing perpendicular or at a certain angle to the plane of the seam, is liable to cause local overheating thus interrupting and splashing the interlayer of liquid solder. Therefore, in soldering, preference should be given to loop coils instead of spiral-helical coils.

The magnitude of the induced current depends on the dimensions of the inductor, coil, and of the space (gap) between the heated parts and the inductor. The space may vary according to the shape of the parts to be heated, and to the rate of heating; with increase in the size of the gap, the heating rate lowers. In soldering, the space may vary between 2 and 20 mm. For soldering thinwalled parts, narrow gaps are more convenient. In order to assure a more uniform heating of irregularly shaped parts, and to prevent fusing of their projections or sharp edges (at radio-frequencies), the gap should be larger than 20 mm. On the other hand, large gaps reduce the efficiency of the coil. A space between the parts and the coil less than 2 mm is dangerous since the loops of the coil are prone to be short-circuited by the parts, the molten solder or the flux, all of which are good electrical conductors. To prevent short-circuiting of the loops during operation, they are enamel-coated or insulated with asbestos cord soaked in water glass /7/.

Thorough penetration of the solder into the gap between the parts to be soldered, requires not only melting of the solder, but also proper heating of the parts in the seam area. Therefore, in selecting the proper induction coil not only its shape, but also the mass of the soldered parts, their heat conductivity and heat capacity should be allowed for.

Due to a certain non-uniformity of heating connected with the induction method (in high-frequency soldering), the character of the volume changes in the parts during heating should also be taken into account. For instance, as a result of heating, the distance between the rod and the bushing around it increases due to expansion of the bushing. In such cases, it is preferable to have the parts heated inside or to use more tight fits for assembling. Apart from the proper shape of the coil, attention should be paid to correct placing since it is most important to start to heat, first, the thick walled parts of the work to be soldered. This will assure uniform heating of the thinwalled parts by heat conduction. Heating of the seam is preparatory to melting and inflow of the solder into the gap (Figure 94).

Soldering of complicated assemblies may be better done in several steps. When the seams are located close to each other, solders of different melting points should be used.

In multiple loop heating coils the loops are usually series-mounted; the induced current has the same intensity in all loops. If one of the loops is used for heating a single piece, it may be shunt-connected, but shunt-connection is liable to produce a heating current of unequal intensity.

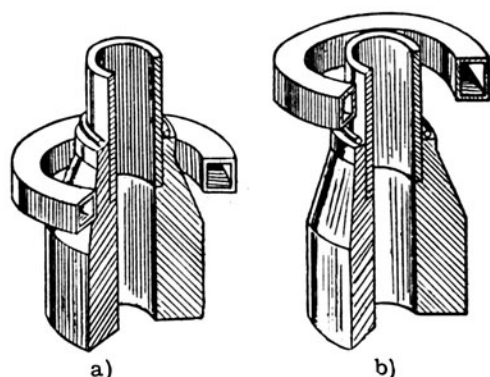


Figure 94. Correct (a) and incorrect (b) placing of the inductor coil beside the soldered seam:
 a) correct placing: the parts are simultaneously raised to the requisite temperature;
 b) wrong placing: overheating and insufficient heating of the thickwalled section is unavoidable

Multiple-loop inductor coils make better use of the full capacity of high-frequency oscillators; however, a non-uniform zonal heating may sometimes occur, which may cause cracks in the soldered parts. In order to avoid zonal heating, multiple-loop coils are made of rectangular cross-section copper tubings, the loops being mounted as close as possible to each other. Non-uniform zonal heating may be diminished by increasing the space between the parts and the inductor coil. When heating flat parts, the current due to the proximity effect, flows along a path simulating the shape of the inductor.

The use of inductor coils permits us to control the degree of heating of different parts of the work to be soldered. Figures 95 and 96 show types of two-loop inductor coils for soldering of hard-alloy tips, and the typical soldered joints.

Soldering technique with induction heating units. In accordance with the design of the parts to be soldered, soldering with high-frequency current may be performed by direct, indirect, or combined heating methods. Direct heating is achieved in the inductor coil proper, indirect heating occurs by heat conduction from a graphite pot or a steel crucible heated by high-frequency current. Current for high-frequency soldering is generated by melt-quench type high-frequency oscillators (Table 77).

When using LGZ-60 or LGP-60 oscillators, soldering should be done with a single valve.

Assembling of the parts in view of subsequent soldering should be done on a support or in an appliance made of heat- and current-insulating materials (refractory bricks, eternite (asbestos-cement), textolite, asbestos-slate, etc).

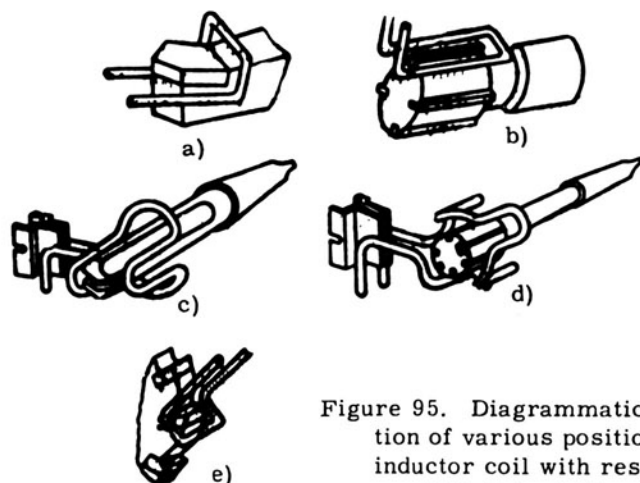


Figure 95. Diagrammatic representation of various positions of the inductor coil with respect to the tool to be soldered:

a- cutters; b- end mills; c- drills; d- reamers and countersink reamers; e- cogs of disk milling cutters.

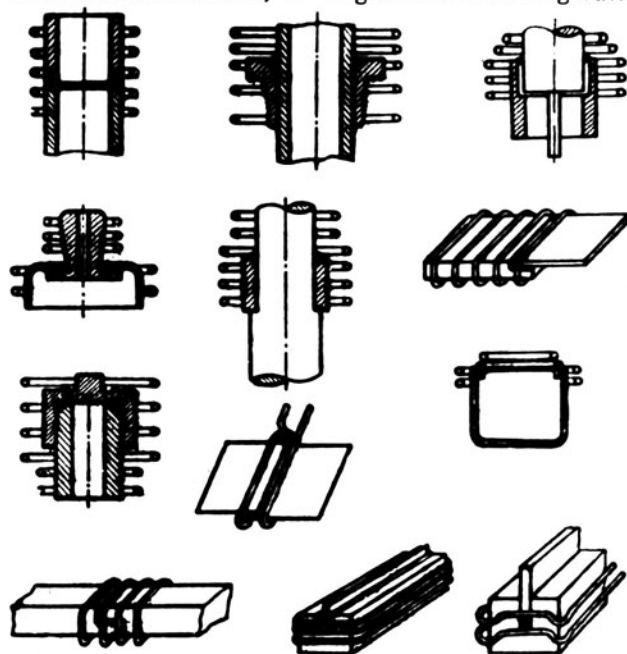


Figure 96. Diagrammatic representation of the inductor coil and the solder during soldering of oddshaped parts

In assembling, the parts to be soldered may be fastenened by different methods: punching, wire binding, pin fixing, binding by foils with notched edges, tack welding (on a spot welder), clamping by special fixtures, or fitting through knurling (Figure 84 d).

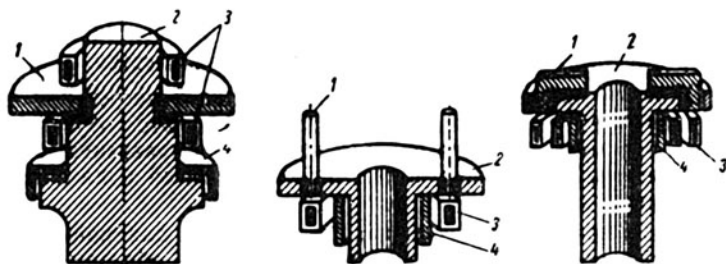


Figure 97. Position of parts 1 and 2, of the inductor coil 3, and the shield 4, in soldering tubular assemblies

In order to strengthen the fastening of the parts after being fixed by the above described appliances (or methods), they may be bound with asbestos cord. For a tighter clamping, parts may be covered with lamellae or small cylinders of electrode carbon, placed between the parts and then bound with asbestos cord. For the same purpose, small plates of asbestos sheets, or rings of asbestos cement may be used, /7/, /8/.

Induction soldering may be achieved more conveniently if the surface of the parts to be soldered is in a vertical or inclined position. The axis of symmetrical parts should be parallel with the coil axis, thus preventing non-uniform heating. During heating of parts intricate in shape, they should be permanently rotated with a speed of 20-30 rot/min. Copper shields 1.5-2.0 mm thick, placed between the parts and the inductor coil, protect those portions which should not be heated (Figure 97) /9/. When soldering thin walled parts, heating should be carried out continuously; soldering of thick walled parts requires intermittent heating in order to level the temperature and to prevent overheating or fusing of projections and sharp edges.

Solder may be applied during assembling, in the shape of foil, wire, or turned rings, powder, cuttings, paste, grains, or sticks. Foil or ring-shaped solders should be placed either in the gap between the parts to be joined, or in special grooves. Usually, the solder is introduced in the upper part of the gap where small grooves are previously machined in the walls of the joint to prevent running out of the solder while melting.

Soldering foils or cuttings if applied above the parts, are liable to be shifted or even completely moved from their place under the action of electromagnetic forces. Therefore, in high-frequency heating, the solder if placed above the parts, should be applied in the form of cuttings mixed with the fluxing material.

High-frequency induction heating may be applied in the soldering of a large variety of parts. This method is particularly convenient in soldering of cylindrical parts. For this reason, induction heating is often used in soldering such types of joints as, pipe joints, flanged socket-tube joints, bushing-axle (shaft) joints, etc. Pipe joints are often made by means of internal or external butt or lap-soldered sleeves (sockets).

In soldering tools, particularly hard-alloy tips, induction-heating methods are largely used, due to their obvious advantages as compared

with other heating procedures; they are used, e.g., for soldering in reverberatory furnaces, in a gas flame, or in electric-resistance welding units.

Type and size of inductor coils for soldering hard-alloy tips are selected so as to assure slow and uniform heating of the soldered joint. The inner diameter of the inductor coil should be approximately equal to or twice the diameter (or thickness) of the soldered part. Spacing between inductor coil and the parts involved should be within 8-15 mm.

For heating tools in the inductor coil, the body of the tool should be heated first, in order to ensure uniform preheating. For this to be done, the seam area is to be heated by heat conduction, and only after reaching a temperature of 700-800°C, the work is to be placed in the inductor coil, taking care to avoid any overheating of the hard-alloy tip. The tip is fastened to its holder by means of manual, foot-driven, or pneumatic clamps. After solidification of the solder, oxides and fluxing residues are to be removed by a steel brush, and the tip slowly cooled at a definite rate (in a furnace, coal particles, salt, asbestos wool, or in open air). After soldering, the tips are sandblasted /8/, /9/.

The induction heating method is also suitable for soldering in a reducing atmosphere or for vacuum soldering.

When soldering is done in a reducing atmosphere, the parts to be soldered are to be placed in a stainless-steel container whose walls and bottom are heat-insulated from the surroundings (Figure 98). The container is then heated in an external multiple-loop inductor coil. Temperature control is assured by means of thermocouples inserted in a special well through the upper cover of the container. Special tubes provided in the upper cover, allow the admission and discharge of the gases. To prevent explosion, the reducing exhaust gases are ignited upon their discharge from the container. If soldering is done in a high-frequency heated container the soldering rate may increase 5-10 times as compared with common electric furnaces having a reducing atmosphere, since heating of the container occurs with extreme rapidity (several minutes); on the other hand heating of furnaces with a reducing atmosphere requires a time-cycle of several hours.

Induction-heating methods are also used largely in soldering of steel and copper parts or in the manufacture of copper and nickel alloy parts.

Owing to certain difficulties in adjusting the temperature within the narrow limits required for soldering most of the aluminum alloys, high-frequency soldering of aluminum and its alloys, is employed for soldering AMts alloys and technical aluminum.

When high-strength aluminum alloys of the D16, D20, DI, or the V95 grades are soldered with solders the melting point of which is close to the solidus of the base metal, the latter are likely to be overheated. Therefore, soldering is to be performed very slowly, heating being done in several stages by intermittent connecting. Heating should be slowed down as soon as the solder begins to flow from the seam area. To assure better penetration of the molten solder into the gap, a repeated short-time connection of the inductor coil may prove to be useful. Rod-shaped solders, molten while in contact with the preheated work, are introduced into the gap, the inductor being cut off.

If aluminum parts are soldered with low-melting solders together

with active fluxing agents, induction heating may enhance a greater corrosion resistance of the joint as compared with the usual flame soldering methods /10/.

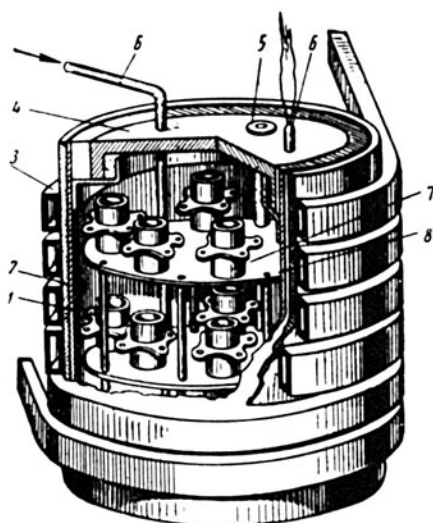


Figure 98. Diagrammatic representation of a container for high-frequency soldering in a reducing atmosphere;

1-body of container; 2-thermoinsulating layer; 3-inductor coil; 4 -cover of container; 5-mount for thermocouple; 6-tubing for admission and discharge of reducing gases; 7-the work to be soldered; 8-support.

Mechanization and automation of the induction soldering process. Quality of an induction soldered joint depends not only on the heating rate but also on the maximum temperature of heating, and on the holding time at this heating temperature. The more stable the heating conditions, the better the quality of the soldered joint, and the more homogeneous are its properties. In order to ensure a stable soldering temperature during induction heating, sometimes a photoelectric pyrometer is connected to the high-frequency oscillator through special relays for automatic switching of the oscillator over a given temperature range. Since photoelectric pyrometers respond only to incandescency of the heated metal at temperatures above 750°C , they are suitable only for soldering steel parts. Their use obviates over-heating of the parts during heating (Figure 99).

When using stable automatic-control high-frequency oscillators, soldering of simple-shaped parts may be achieved through a special time relay for switching the heating system at a given time interval

Heating intensity may be controlled also by means of a special power-relay requiring constant sizes of the parts to be soldered, a permanent

clearance between the parts and the inductor, and a definite heat-output. Under such conditions, this method assures optimal maintenance of constant heating conditions but, owing to a certain lack of suitable devices did not gain wide acceptance.

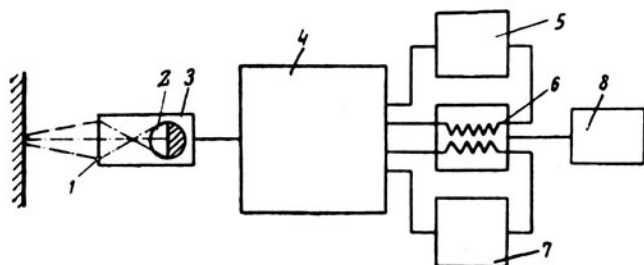


Figure 99. Diagrammatic representation of the FP-3 photoelectric pyrometer:
1-objective; 2-photoelectric cell; 3-telescope; 4-photo-cell amplifier; 5-measuring instrument; 6-polarized relay; 7-resistor of the unit; 8-control relay.

Continuous automatic feeding of the parts to be soldered requires a constant speed of the feeding conveyer. In this way, for instance, condenser bottoms are soldered in conveyer units. In such cases, the inductor, 300 mm in length, consists of two tubes through which the current, generated in a high-frequency oscillator of 4 kw and 400 kc, flows in opposite directions. The conveyer consists of an endless rubber belt provided with bakelite supports for the parts to be soldered. Speed of the belt is 3 m/min; output of the soldering unit is 2500 condensers per hour /11/.

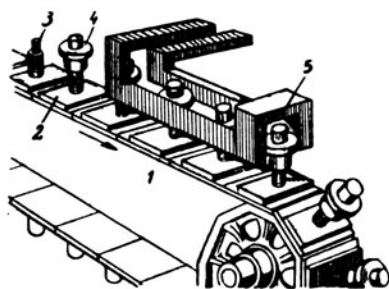


Figure 100. Induction-heating soldering in a continuous automatic-feed high-frequency unit:
1-conveyor belt; 2-ceramic base; 3-supports for the parts to be soldered; 4-supports for ready soldered parts; 5-inductor coil.

The parts to be soldered may also be intermittently fed to the induction unit by means of automatic devices which connect and interrupt the inductor coil at a given holding time.

In order to assure continuous heating of steadily delivered parts, the shape of inductor coil should be chosen so as to permit such a movement of the parts. Usually, the inductor coil has no side walls. Figure 100 depicts an automatic unit for soldering of cutting tools.

Delivery of the parts to the inductor coil may be accomplished by various devices. Most commonly used is the straight-line track conveyer or the rotating-disc conveyer, the parts being fastened on the surface of the latter and alternately fed to the induction unit /8/, /12/.

When feeding of the parts to be soldered is accomplished through the rotating-disc conveyer, the inductor coil should permit variation of current density in different parts of the work to be soldered, thus assuring uniform heating throughout the soldering process. For this purpose, special shaped inductor coil copper tubes having different cross sections have been designed. In soldering cutters in similar coils, the body of the cutter is heated first, followed by heating of the cutter head.

§ 2. Electric-Resistance Soldering

Due to the Joule effect, the heat generated when a current flows through the parts to be soldered, or through electrodes being in contact with the parts, may be used for heating the parts in view of their subsequent soldering. Heating may be achieved either due to the heat generated as a result of a great contact resistance on the borderline between the parts and the solder, or due to an intense heating of the electrodes while in contact with the parts to be heated.

Low-voltage and high-amperage current, obtained usually from the welding transformer of electric-resistance welding units, is best suited to this purpose. Therefore, electric-resistance soldering is often carried out in spot welding or butt welding machines, feeding of the current, and clamping of the parts to be soldered being done by means of electrodes (Figure 101). The same principle applies also to certain electrical-soldering machines and devices, e. g., hand spot-welding tongs (pliers). These machines and devices usually consist of a special transformer, the secondary of which being connected by hand or automatically to the clamping electrodes. These electrodes are usually made of copper and provided with water cooling just like in welding units. Heating of the seam area takes place due to the intense transient resistance between the parts and the solder. The magnitude of the transient resistance depends, heating time and current intensity being equal, on the pressure exercised on the parts, i. e., on the area and specific gravity of the clamping electrodes. After melting of the solder, the transient resistance suffers a sudden drop; further heating is now accomplished due to the electric resistance of the work, which increases with the increase in temperature (Figure 102).

Material for electrodes may be graphite (EG2, EG8 etc), or heat resisting steels and alloys (EI437, Kh30, Kh18N25S, Kh12M, etc), (Figure 103).

Electrodes of different materials (e. g. graphite and tungsten) permit the heating of semi-accessible places of parts having different thermal conductivity and electric resistivity.

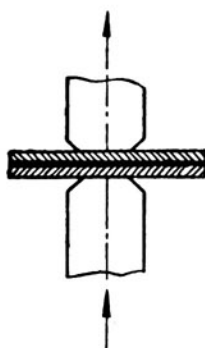


Figure 101. Position of solder and soldered parts between the electrodes of a spot-welding unit used in resistance soldering

Choice of proper electrodes for various materials, joints or cross-sections, is chiefly done by experiment, the electrodes being selected in various shapes and assemblies according to the specific requirements of the work.

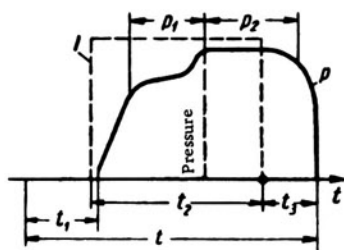


Figure 102. Sequence diagram of current-connection and of applying the pressure p : p_1 - pressure at the beginning of soldering; p_2 - idem at the end of soldering; t_1 - duration of assembly; t_2 - duration of heating; t_3 - duration of cooling; t - total time-cycle of soldering.

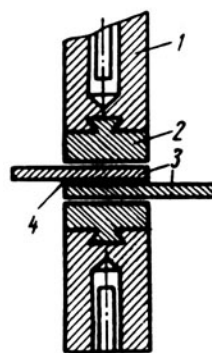


Figure 103. Position of solder and parts to be soldered in resistance heating by means of carbon lamellae fixed to the electrodes of a spot-welding unit: 1-electrode; 2-carbon insertions; 3-the parts to be soldered; 4-solder.

Lamellae, sectioned from burned graphite electrodes of electric melting furnaces, or from the graphite brushes of electric machines may furnish the stock for electrodes. Due to a certain brittleness of graphite electrodes, they need no stronger fastening of the parts to be soldered, than in case electrodes of heat-resisting alloys and steels are used.

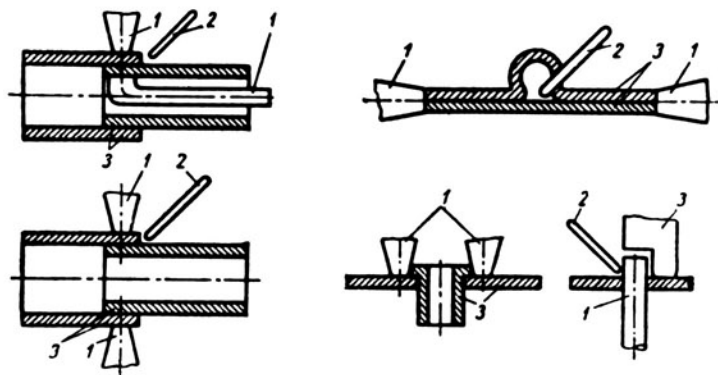


Figure 104. Position of electrodes (1), of the parts to be soldered (3), and the solder (2) in electric-resistance soldering

Soldering of parts intricate in shape may be done by feeding the current from the network to a graphite plate on which the work is placed, the latter being connected to the other terminal of the network. The current, while flowing through the parts to be soldered and the graphite plate, causes heating of the parts. Heating occurs chiefly due to heat conduction from the heated graphite plate. Figure 104 illustrates some instances of correct placing of electrodes during soldering. The work may be fastened by means of special fixtures not connected to the source of electric current (Figure 105).

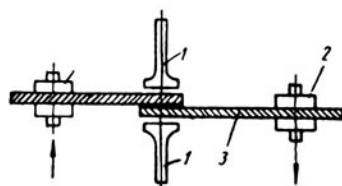


Figure 105. Position of solder and the parts to be soldered (plates) in resistance-heating units; the clamping devices are insulated:
1-clamping; 2-current-feeding terminals; 3-the work to be joined.

The salt fluxes used in soldering with high-melting solders are dielectrics in the solid condition. Therefore, in resistance heating when the current flows perpendicularly to the seam area, the flux should be rendered electroconductive by dissolving it in water or alcohol. If the flux is fluid it is to be applied right before soldering, to avoid evaporation of the solvent prior to switching on of the current.

The method of fastening the parts between graphite electrodes fixed in the copper holders of the welding unit is most widely used in resistance soldering; another heating method provides fastening of the parts between electrically heated graphite or metallic plates.

When soldering is done between copper electrodes, the parts to be soldered should not differ in their thermic and physical properties, since otherwise, the heating nucleus is liable to shift from the place of contact to one of the parts or even to the electrode.

Similar difficulties may arise also in soldering parts of different thickness. This particularly refers to soldering structurally complicated joints of conductors to plugs, of rotor rings, of stator windings, etc.

Electric-resistance soldering by means of graphite lamellae fixed to the copper electrodes of the welding unit, is achieved in the following manner. The foil-shaped prefluxed solder is inserted into the gap between the parts, their surface being suitably prepared for soldering. During heating the lateral surface of the parts placed between graphite electrodes should be sprinkled with a borax solution to reduce burning of the electrodes. On the other hand, the flux should not contact that part of the electrodes which touches the parts to be soldered; therefore, the amount of fluxing material applied on the parts should not exceed a minimum value /13/, /14/. Service life of graphite electrodes depends on the working conditions. Resistance soldering requires low-voltage and high-amperage current. Feeding of current is sometimes interrupted, in order to ensure a more uniform heating of the parts. After completing the melting and running in of the solder, the current is switched off and the pressure is not released until the solder is completely solidified.

When the time-cycle of electric-resistance soldering is relatively large, melting of solder can be better controlled and the current easily switched off by means of the foot-lever at any desired moment.

When the time-cycle is much shorter (less than 0.5 sec) one may fail to switch off the current rapidly by means of the foot-lever; in such cases it is more suitable to use a high-voltage relay or a special interrupter. Stable clamping of the parts to be soldered (in repetition work), may suitably be obtained by means of an adjusting spring-coil.

This procedure applies chiefly to soldering with high-melting solders (silver, brass, phosphorous copper, etc); it may also be used for soldering copper strips required in the manufacture of windings for additional poles of the welding units. This is better done in a special soldering machine having a transformer of 15 kva; current is applied from this transformer to the soldering tongs provided on the ends with iron plates, on which graphite plates are fastened. Secondary voltage on the tongs varies from 3 to 4.3 volts, and the current, from 100 2300 amp /15/ and /16/.

Soldering of stator windings and rotor rings is carried out on a special appliance mounted between the electrodes of the spot-welding unit (Figure 106). This appliance comprises a transformer, a rotating table and an electrode holder /17/. The primary of the transformer is energized from a low-voltage supply of 380 v. In soldering, the intensity of current attains

2000-3000 amp. Material for solders is phosphorous copper, for flux-borax. Sometimes self-fluxing PSr71-28-1 solders are used as well.

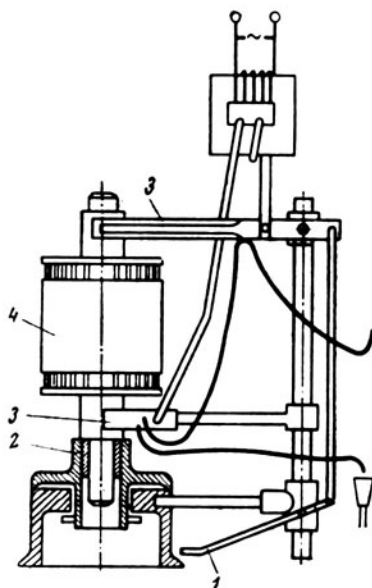


Figure 106. Appliance for soldering rotor rings and stator windings, mounted between the electrodes of a spot-welding unit:

1-lever; 2-support; 3-the work to be soldered

The work to be soldered is placed on the rotating table.

The ends of the work together with the solder are clamped between the graphite electrodes of the soldering head, and the current starts to flow. Only after complete melting of the solder and formation of the required joint, the electrodes are unclamped.

This method is applied for soldering tungsten lamellae to copper parts in a hydrogen medium delivered to the parts through a perforated tube coiled round the work, the openings being directed toward the work. After solidification of the solder, the electrodes are released /18/.

If foil-shaped solders are not available a wire similar to that employed in flame soldering may be used. For this purpose the parts to be soldered are prefluxed and placed between the electrodes of the spot-welding unit. After proper heating the electrodes and the parts to the soldering temperature, the end of the soldering wire should be clamped to the surface of the parts near the gap, until the molten solder fills the gap completely.

Soldering of parts of small cross-section e.g., wire, cable terminals, etc, is done with special soldering tongs /tweezers or pliers/ (Figure 107).

These tongs are connected to the transformer by means of two flexible conductors, 6 mm² in cross-section. The applied voltage and current can be adjusted over a range from 5 to 40 v and 20 to 200 amp, by proper selection

of the connecting terminals. Weight of the soldering tongs is 250 g, their length, 27 cm. Control is accomplished by means of special push-keys. The clamping force on the electrodes may be varied within 400-3500 g. The electrode holders of the soldering tongs are fitted with special copper-plated carbon electrodes.



Figure 107. Tongs for resistance-soldering

A special appliance mounted on the handles of the tongs, permits adjusting the clearance between the upper and lower electrodes and the pressure applied on them.

Soldering by means of such tongs is extremely simple: a prefluxed foil-shaped solder is placed between the parts to be soldered. Preferably, the flux should be in the liquid condition; fluxing substances leaving solid residues (e.g., borax) are less suitable. The parts to be soldered are clamped between the tongs and connected to the voltage supply. After melting of the solder, the current is cut off by means of the foot lever, and the tongs released.

Such tongs are also suitable for soldering with low-melting solders. Unlike the electric soldering bit, they offer a uniform heating of the work and reduce the appearance of the defect of cold shut /cold set/.

These special soldering tongs equipped with carbon and copper electrodes are applied for soldering commutator lugs in electric machines, with cadmium and copper phosphorous solders. This soldering method obviates overheating of the metal on the seam area and damaging of the insulation. In assembling such parts, the foil-shaped solder is applied either by fixing, or by tack-welding to the seam area, the adjacent lugs being previously bent. The soldering seam (seam area) is then clamped between the soldering tongs, and the current is switched on; after melting of the solder, the current is automatically cut off; the soldered joint and adjacent insulation are then cooled by an air jet.

The mechanical strength of such types of soldered joints differs little from joints soldered with low-melting solders /19/.

Soldering of wire ends (lugs) of armature windings of electric generators, may be done by heating the parts to be united, in an electric resistance soldering unit. For that purpose, one of the electrodes having the shape of a plate is clamped to the commutator ring (segments), the other electrode is directly connected to the lug of the same ring or of the adjacent one (Figure 108).

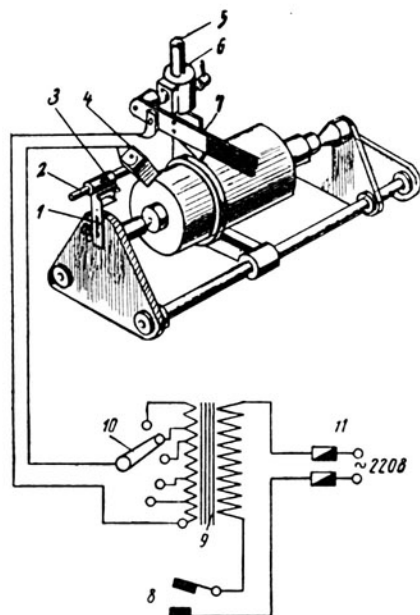


Figure 108. Diagrammatic representation of the setup for resistance soldering of the wire ends (lugs) of the armature windings:

1-swinging lever together with the carbon heating element; 2-bar; 3-bushing; 4-copper contact lamella; 5-and 6- brackets; 7-spring; 8-fuses; 9-transformer; 10-connecting foot lever; 11-commutating switch
(According to A. B. Slonimski)

Soldering by heating the work between copper electrodes of resistance welding units is employed e. g., in the manufacture of sintered-metal contacts, hard alloy tips (of cutting tools), and band saws.

All metal-electric contacts (i. e., conductor joints) used in various electric installations and equipment, differ from terminal contacts in that they possess a constant resistivity.

Electric contacts soldered with high-melting solders of the PSr45, PSr70 type, or with copper-phosphorus solders, are most reliable. Soldering of such contacts is better done in low-power spot-welding units and special setups based on the same working principle (e. g., the TsPK-LA unit) /20/.

Electric resistance-soldering of silver, sintered metallic, and other contacts is usually made in units provided with copper, bronze or brass current-carrying parts separated by a solder interlayer. If the work to be joined has great variations in its thermal and physical properties, heating of the seam area may prove to be a difficult task as the zone of maximum

heating is liable to shift to the electrodes. Therefore, choice of electrodes for electric-resistance soldering of electric contacts should be done bearing in mind the thickness and thermal and physical properties of the parts to be soldered.

Soldering of electric contacts to copper or copper plated parts, or to phosphorous-bronze parts, is done with self-fluxing solders. Best soldering alloys are the following: PSRMF-71-28-1 ($71 \pm 0.5\%$ Ag; $28 \pm 0.5\%$ Cu and $1 \pm 0.21\%$ P), with a melting point of 770°C and a soldering temperature of 800°C . This low-melting solder replaces the high-melting solder of the Cu-7% P alloy, whose melting point varies within $750\text{--}800^{\circ}\text{C}$.

The thickness of the copper-plated layer on copper alloys should be 4-7 microns and on steel, 15-20 microns.

Galvanized, nickel-plated and chromium-plated contacts should not be soldered with self-fluxing solders /20/.

Soldering of contacts to non-plated brass or bronze parts implies use of fluxing material (e.g., borax). For this purpose, soldering may be done with a mixture of solder and flux, ground to a fineness of 100-200 mesh screen and composed of 3 parts solder to one part flux. If soldering contacts to brass or bronze parts with the PSRMF-71-28-1 solder, a saturated aqueous solution of borax may be used.

Electric-resistance soldering is used extensively in soldering blades of band saws. Special machines equipped with monophasic transformers, which are essentially a variety of the low-power resistance-welding units, have been devised for this purpose. The terminals of the secondary circuit of the machine are connected to brass or bronze electrodes having the shape of small plates $10 \times 40 \times 120$ mm in size; the blades to be soldered are fastened between these electrodes and then heated by passing current through the seam area /21/, /23/.

The soldering process occurs in the following manner. A bronze foil 0.05 mm in thickness or a silver or copper foil-shaped solder is placed between the bevelled edges of the broken ends of the saw blades. The bevelled blade-edges then are clamped and covered with borax; heating up to $800\text{--}850^{\circ}\text{C}$ is achieved by passing electric current through them. Just before finishing heating, the seams are clamped by a special device (Figure 109) in order to squeeze out excess solder; the ends of the blade are then quenched. After soldering, the soldered joint is subjected, in the same unit, to tempering followed by air cooling, straightening, setting and sharpening. The same procedure applies also to joining of watch and gramophone springs, knives, cooking-stove burners, etc /24/.

If the parts of the work to be soldered differ markedly in size and in thermal or physical properties, those parts greater in mass, should be heated additionally. For this purpose, additional current may be supplied from a winding, through swing terminals. Preheating may be done also by means of an electrically heated, thermostable steel plate.

Resistance soldering may be achieved not only on a spot welder but also on a small power seam-welding unit.

As it was found, the electrical-resistance method may be applied also in soldering of titanium parts /25/. For such instances, pure silver solders (in the shape of foils of 25 mm thick), or pure copper solders (0.025 mm) may be suitable. Soldering is to be done in an inert, high-purity argon ($0.0002\text{--}0.0003\%$ O_2), atmosphere.

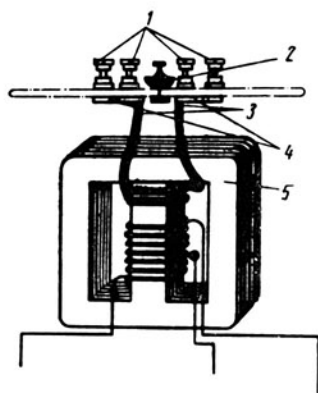


Figure 109. Wiring diagram of electric resistance unit for soldering band-saw blades:
1-and 2- springs; 3-secondary winding of the transformer; 4-current feeding supports; 5-transformer.

It is interesting that in soldering titanium and its alloys, favorable results were obtained only after repeated heating.

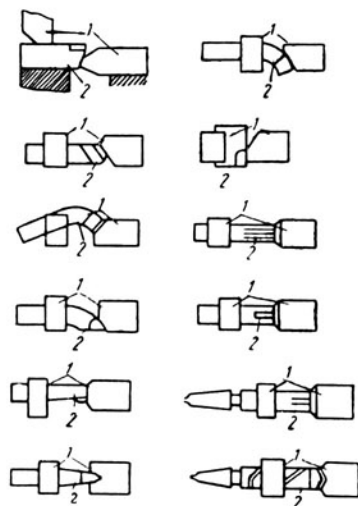


Figure 110. Diagrammatic representation of position of electrodes and tool parts during resistance-soldering:
1-electrodes; 2-the work to be soldered.

Electric-resistance, spot and seam-welding units may be used also in soldering of molybdenum and tungsten parts. Soldering of molybdenum sheets is done with foil-shaped nickel or tantalum solders. In order to avoid oxidation of tantalum, the soldering electrodes should be water cooled.

Tungsten parts are soldered with silver, copper or nickel soldering-foils or with other heat resistant foil-shaped solders. With a thorough cleaning of the surface of the parts to be joined, soldering may be done without any fluxing substance. Soldering of joints subjected to high temperatures may be performed with tantalum soldering-foils /26/.

As previously stated, electric-resistance methods may be applied in soldering of hard-alloy tips /27/. In such instances, heating may be carried out according to the diagram in Figure 110. Prior to resistance soldering, the contact face of the electrodes should be thoroughly prepared thus assuring maximum contact with the parts to be soldered. Any incomplete contact between the electrodes and the parts, leads to overheating. In soldering hard-alloy tips, overheating is liable to produce cracks.

§ 3. Electrolytic Soldering

Soldering in electrolytic baths is based on the fact that a cathode immersed in an electrolyte, is heated when an electric current is passing through that electrolyte. This phenomenon was first noticed by Fizeau and Foucault in 1884. Technical principles of this heating method for soldering purposes have been laid down in 1892-1896 in the patents of Lagrange and Hoho /28/ and of H. H. Benardos /29/, /30/.

Lagrange and Hoho suggested applying the electrolytic-heating method* in heat treatment of steel, glass or other materials, in welding and soldering of metals and alloys. According to these authors, the work (i. e., the cathode) may be heated in an electrolytic bath (anode), in an electrolytic jet, or by contact with a damp, porous material filled with an electrolyte.

In his invention termed "Hydroelectric melting and heating of metals" N. N. Benardos suggested heating metal in an electrolytic jet, delivered by means of a device similar to the common soldering tool. According to Benardos, aqueous electrolytes should be suitable for this purpose. He recommended this method for electroplating of metals, heating of parts prior to their hot working, casting small steel parts, hardening and annealing, welding, smelting of alloys, surfacing (building-up) of casting defects, etc.

Lagrange and Hoho, and Benardos as well, believed that the intense heating of the cathode in an electrolyte through which direct current is passing, is due chiefly to the high resistance of the gas and vapor envelope surrounding the cathode.

In the USSR, I. Z. Yasnogorodskii first started (in 1949) practical use of electrolytic heating in the hardening of steel parts and soldering of magneto terminals /31/. He first devised special machines for electrolytic heating.

A paper published in 1954 in Czechoslovakia reported on the experience gained in connection with this method applied to welding and soldering of metals /32/.

The processes occurring when an electric current is passing through an electrolyte causing heating of the cathode, are rather complicated and little investigated. When a direct current is passing through an aqueous

* [Termed also galvanic polarization heating].

electrolyte in which the work to be heated (cathode) is immersed (the metallic electrolyte containing bath being the anode) three stages may be noticed.

If the voltage is raised to a definite value, intensity of the current passing through the electrolyte will be expressed (according to Ohm's law) by the formula:

$$I = \frac{E - e}{R},$$

where E = voltage between the electrodes; e = polarizing voltage;
 R = resistance.

In the very first stage of the process, the cathode is heated only slowly but the process is associated with electrolysis of the aqueous solution, and evolution of hydrogen at the cathode. Hydrogen ions and water vapors, forming a kind of "jacket" around the cathode, constitute the proper medium for the processes, making possible heating the cathode to the requisite temperature.

By further raising of the voltage, the amount of hydrogen evolved at the electrodes, suddenly increases, thus promoting a local separation of the electrolyte from the electrode. This results in formation of a peculiar liquid bridge between the electrolyte and the cathode surface. High-amperage current while passing through this bridge causes heating and boiling of the electrolyte, and formation of an aqueous phase. The layer of hydrogen ions and water vapor offer additional electric resistance thus reducing the current intensity.

$$I = \frac{E - e}{R - r},$$

where r = resistance of the continuously appearing and disappearing electrolytic bridges.

This is the second stage of the process. It is marked by an increase in the temperature of the cathode, and by unstable working conditions.

With a further rise of voltage and after the cathode reaches definite temperature, steady working conditions are established between the cathode and its surrounding envelope. Owing to spark discharges between the cathode and the gas layer, the latter becomes luminescent; the gas layer acts as a condenser. The hydrogen ions strike the cathode, their kinetic energy causing an intense heating of the cathode. This is the third stage of the process.

According to some authorities /31/, /32/, during the third stage, in the gas envelope surrounding the cathode, certain exothermic processes are likely to take place, providing an additional heat source; this assumption is still to be proved.

Electrolytic heating may raise the temperature of the cathode to a high value; so, for instance, electrolytic heating offers sufficient intensity for welding molybdenum to steel parts.

Heating conditions in an electrolytic medium depend on the composition and temperature of the electrolyte, on the density and voltage of the heating current, and on the heating time.

Suitability of electrolytes for heating purposes is governed by the amount and conditions of hydrogen evolution throughout the stages of the

process. Most suited are electrolytes which, at a reduced current density, cause abundant evolution of hydrogen at the cathode. Such electrolytes are: aqueous solutions of salts, acids and alkalies, the cations of which may be found at the beginning of the scale of electrostatic tension related to hydrogen, solutions of alkaline compounds, acid or alkali solutions like, Na_2CO_3 , Na_2SO_4 , NaOH , KOH , HCl etc. Metallic compounds of Ca and Mg, having a larger electrostatic tension than hydrogen, are unsuitable, since in the first stage of the process (electrolysis), hydroxides of these metals, insoluble in water and hindering evolution of the process, precipitate on the cathode. Therefore, when using electrolytes containing Ca or Mg salts, the intensity of the current required for heating will be higher when using electrolytes of another composition. Solutions of metallic compounds, with an electrostatic tension lower than that of hydrogen, do not afford stable conditions for the third stage and are less suitable for heating purposes.

The concentration of electrolytic baths is a decisive factor in the evolution of the different stages of the process. The cathode starts to heat up only at a certain concentration of salts, acids, or alkalies. So, for instance, when using an aqueous solution of sodium carbonate, frequently employed in electrolytic heating of metals, heating of the cathode at a voltage of 220 volt, may be achieved only if the concentration of the salt is not less than 4%. In an electrolyte with a smaller concentration of Na_2CO_3 during the passage of electric current only the first and second stages of the process occur. In a hot electrolyte the electric resistance of the gases increases and the concentration of Na_2CO_3 , may be less than 4%.

However, it is not practicable to heat the electrolyte above 80°C , since the gaseous envelope round the cathode is liable to be destroyed by evolving vapors.

At present, heating is achieved in electrolytes composed of 10-15 % aqueous solution of Na_2CO_3 at $50-70^\circ\text{C}$; these solutions assure a stable heating of the cathode and do not corrode the steel parts to be heated.

Usually direct current is required in electrolytic heating since alternating current, though it heats the cathode, may lead to an unstable process, and to splashing of the electrode. Apart from this, when using alternating current, the current density on the electrodes is smaller than in using direct-current heating. Therefore, at the same current intensity, alternating current allows heating of parts of a smaller area than direct current of same intensity.

Heating of the cathode starts upon reaching a certain voltage. Voltage of soda solutions /33/, for heating steel parts, should have a minimum value of 170 v.

The current density on the electrodes is of utmost importance for the heating of the cathode. Luminescence of the gas envelope is observed at that electrode, where the current density is greater, and the contact surface with the electrolyte is smaller. Luminescence of the gas envelope of the anode is not associated with an intense heating, as in luminescence of the hydrogen envelope of the cathode. Therefore, in electrolytic heating of parts (cathode), the current density on the surface of the parts should be larger than on the surface of the anode. Consequently, the surface of the parts to be heated should be slightly smaller than the surface of the

anode. In this case, the area of the metallic bath (container) imposes certain restrictions on the sizes of the surface to be heated.

Table 78

Effect of the depth of immersion of the anode on the character of the process in the electrolytic baths

Immersion depth of anode, mm	Intensity of current, amp.	Characteristics of the process
1	1	Anodic luminescence
2	1.8	The same
3	2.0	" "
4	2.3	" "
5	3.0	" "
6	3.5	Anodic luminescence
7	3.5	The same
8	3.8	Temporary flash on the cathode
9	13	Stable luminescence on the cathode

Table 78 presents some data about the effect of the immersion depth of the anode, and on the characteristics of the process going on in the electrolyte during passage of current /31/. The cathode and anode used in those investigations, were made of 10 mm diameter steel, and cylindrical in shape. Immersion depth of the cathode in the electrolyte was 5 mm.

Electrolytic heating is suitable for solid conductors such as, steel, cast iron, brass, aluminum, graphite, etc. Heating conditions of various materials in electrolytes, depend on the thermal conductivity of the materials involved but not on their electric and magnetic characteristics.

In a series of investigated materials, heating of the cathode starts at the same current density and voltage, regardless of the electrode material /33/. Any further rise in voltage and intensity, increases rate and intensity of the heating process (Table 79).

As shown by Table 79, heating of steel, aluminum or brass requires a current of sufficiently high voltage and amperage, i.e., the power of a large d.c. generator. So, for instance, heating of a steel cylinder with a surface area of 100cm², to 700-800°C requires a d.c. generator of 40 kva, which largely limits the application of this method.

In electrolytic heating, the current density is non-uniformly distributed, particularly in irregularly shaped parts with sharp edges or projections on which current density is higher than in other places. A non-uniform current density on the surface of the parts to be heated may lead to overheating or fusing of sharp edges or projections of the parts. In order to minimize the current density on such portions, they are to be shielded. Shields are suitably made of refractory and insulating material, e.g., of refractory brick. By properly fitting the shape of shields, the current density on the surface of the parts to be heated may be levelled accordingly. Shielding does not require a tight contact between the shield and the parts; a distance between them 2-3 mm in size is allowed for. The shield should approximately simulate the shape of the surface to be covered (shielded). Electrolytic heating of metals is associated with electroerosive phenomena.

So, for instance, when a steel strip, 0.6 mm thick, immersed in an electrolytic bath to a depth of 2-3 mm, is exposed to a voltage of 140 v, it will be destroyed at a rate of 0.001 mm/s.

Table 79

Effect of voltage and current density on the intensity of electrolytic heating

Voltage in v	Current density in amp/cm ²	Characteristics of the processes
150	Steel 4.3	Cathode is not heated. Periodical appearance of luminescence.
175	1.74	Reduced heating. Stable luminescence and visible gaseous envelope.
200	1.99	Heating up to 700°C, at depth of 15 mm.
225	1.97	Heating up to 800°C, at depth of 25 mm.
250	2.10	Heating up to 850°C, at depth of 20 mm.
	Brass	
157	4.0	No heating. Periodical appearance of luminescence.
175	1.75	Stable luminescence and visible gaseous envelope.
200	1.95	Heating up to 700°C, at depth of 20 mm.
225	1.97	
250	1.85	Uniform heating up to 750°C at a depth of 40 mm (of the immersed and non-immersed portion of the work).
	Aluminum	
125	4.00-1.65	After a certain period (30 sec), formation of stable luminescence. Accordingly, reduction of current density (from 4.00 to 1.63 amp/cm ²).
150	1.98	No heating. Periodical appearance of luminescence.
175	1.98	Reduced heating.
200	1.98	Heating up to melting.

At present, the following electrolytic methods of heating metals have gained acceptance: immersion in an electrolytic bath, heating in an electrolytic jet, and heating by contact with a porous insulator through which the electrolyte is fed.

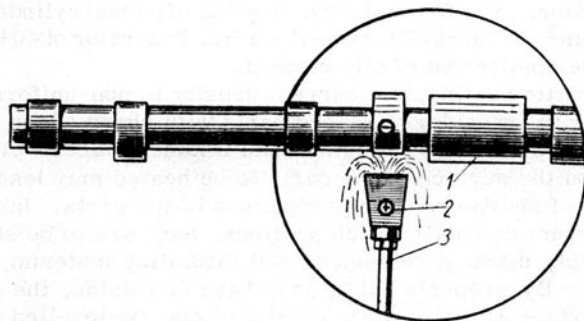


Figure 111. Diagram of heating in an electrolytic jet:
1-the parts to be heated; 2-electrolyte;
3-tube for delivery of the electrolyte.

At present, electrolytic heating of metals is principally applied in heat treatment of steel parts, for which definite working conditions are already available. This method may be used also for soldering of small-sized parts. Electrolytic heating of metals may be achieved by partial or total immersion of the parts in the electrolytic bath. Figure 111 illustrates the method of heating in an electrolytic jet. The current density on the surface of the work to be heated, is stronger, the shorter the jet, but the distance between the feeding tube (pipe) and the part should be sufficiently large to prevent appearance of a short-circuit. For this purpose, the end of the feeding pipe is usually covered with a tip of porcelain, quartz, or another similar material.

Heating of cylindrical steel pivot-journal, 55 mm in diameter, to 850°C , is done with a 10% aqueous solution of caustic soda. The electrolyte feeding-pipe is 12 mm in diameter; the distance between pipe and part is 20-30 mm; power consumption for heating is 7 kva; heating time is 120 sec. During heating, the work should be continuously rotated with a speed of 30-40 rot/min. The same electrolyte may be used as a cooling medium in quenching operations.

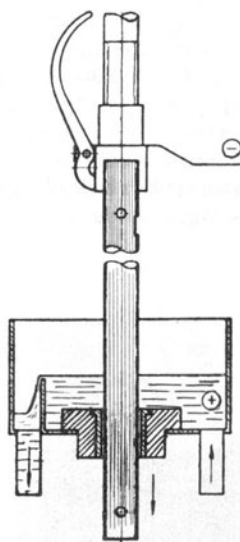


Figure 112. Diagrammatic representation of heating phases in an electrolytic bath

Heating of parts intricate in shape, is more conveniently done by the indirect contact-method in which the electrolyte is fed to the parts through a porous refractory insulator. For this purpose, spongy fire-clay is best suited; a piece of such clay, wetted by the electrolyte, is placed on a metallic frame connected to the positive pole of the circuit. Heating occurs at the places of contact between the fire-clay and the work.

By application of continuous electrolytic heating with a current of relatively reduced intensity, the sizes of the work to be heated may be increased. Figure 112 shows a schematic representation of the heating phases in an electrolytic bath. On the bottom of the container a ceramic bushing is mounted; the parts to be heated pass successively through the bath and the bushing. The clearance between the parts and the bushing varies within 1-2 mm. The electrolyte is prevented from running out from the bath, due to formation of a gas and vapor envelope in this clearance, during passage of the work to be heated. This method is well suited for spot and zonal heating (using thereby lateral shields).

Sheets, strips or discs may be successively heated, using special shielding plates to cover the front ends of the parts. To avoid fusing of the edges of the parts during heating, the length of the slot in the shielding plates should be 1-2 mm smaller than the width of the parts.

At present, a series of devices have been designed, which permit automation of electrolytic heating. These automatic devices may be used also in soldering. Figure 113 depicts the general view of the AE-4 automatic unit used for soldering magneto terminals. Soldering is made by shielding either the front end of the magneto, or the terminal. These methods are particularly suited for fastening the members of a joint prior to its soldering. The heating method involving shielding the fixed terminal is more convenient for soldering than is the method with shielded front ends. Soldering may be done at a voltage of 180-200 v, and an amperage of 6-8 amp. Heating time (up to 1100°C) is 8 sec. Height of the electrolytic bath above the immersed screw head is 4-6 mm. The joint soldered by electrolytic heating has a width of 0.1-0.2 mm, whereas the width of a joint soldered in furnaces with a reducing atmosphere (hydrogen) varies within 0.12-0.8 mm. Electrolytic heating produces tight soldered joints without any oxide inclusions.

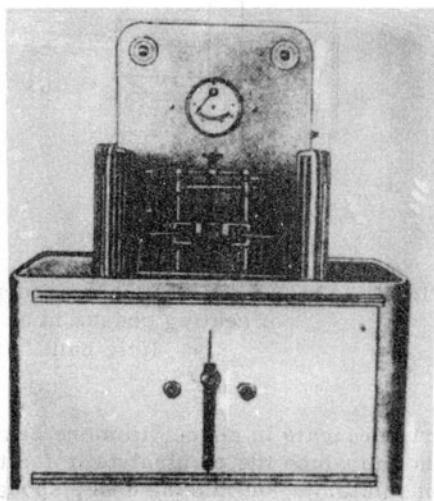


Figure 113. External view of the AE-4 automatic soldering unit

Electrolytic soldering compares favorably with other soldering methods since it allows the uniting of dissimilar metals, the oxides of which are capable of being reduced in a hydrogen atmosphere. The large heating rate, together with automation, offers high efficiency of the process and high quality of the soldered joint.

One of the disadvantages of this method is, that it is suitable only for heating small and simple parts.

§ 4. Electric-Arc Soldering

Electric-arc heating is employed in soldering small parts of various devices. In this method the electric arc may be induced between the soldering foil placed in the gap between the parts to be joined, and a graphite or carbon electrode, or between the parts and the soldering electrode /34/-/39/. Fusing of solder and heating of the metal in the gap area occurs under the action of heat generated by the electric arc. Current may be furnished either from a battery or from the general voltage supply, the voltage being previously lowered by a step-down transformer. The latter method is used in soldering stator or phase rotor windings with phosphorous copper solders (7% P, and the remainder, Cu).

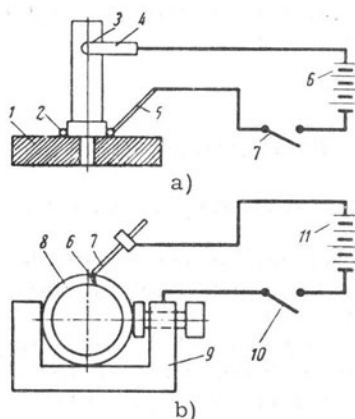


Figure 114. Diagram of electric-arc soldering:

a-soldering of a brass dowel to a ceramic plate; b-joining of a ring-shaped part;
1-plate; 2-ring; 3-dowel; 4-terminal;
5-electrode; 6-seam area; 7-solder;
8-the part to be soldered; 9-appliance;
10-push-button switch; 11-battery.

Soldering is done in the following manner. Pieces of foil-shaped solder ($4-6 \text{ mm}^2$) are placed in the gap between the parts to be united. Carbon electrodes (10-12 mm in diameter) or graphite electrodes (6-8 mm)

required in soldering should be made of carbon or graphite. The electrodes are cone-shaped, the length of the cone portion being twice the diameter.

One of the poles of the current supply is connected to the support by means of pliers or another appliance touching the part; the other pole is connected to the electrode. The current induced between the carbon electrode and the soldering foil, melts the foil which flows into the gap. Soldering of stator windings requires a length of the arc of 4-5 mm (at an amperage of 75-100 amp). The soldering rate is proportional to the amperage.

Windings of phase rotors are soldered by means of carbon electrodes (18-20 mm in diameter) at an amperage of 200-350 amp.

In soldering devices and electrical equipment, the heat generated by the electric arc is liable to damage the insulation close to the seam area. In order to prevent overheating of the insulating material, refractory shields are used.

Electric-arc heating is used in soldering brass dowels to a ceramic plate, the ring-shaped solder being previously placed around the seam area. The current delivered from a battery flows through the terminal 5, the dowel 1, and the solder 3 (Figure 114). By closing the circuit due to the contact between the electrode and the solder, an electric arc is induced, which melts the ring-shaped solder.

Electric-arc heating may be used, not only for soldering with high-melting solders, but also with low-melting solders. In this case, the solder should not contain components having a high evaporation pressure, such as, zinc or cadmium, since they are liable to melt and evaporate instantaneously under the action of the electric arc.

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Chapter XIII

TINNING AND SOLDERING BY FRICTION METHODS

Friction soldering is sometimes termed also, soldering by rubbing, by shaving, or abrasive soldering.*

In this method of soldering, the solder heated at a temperature higher than the solidus, is applied on the surface of the parts to be soldered and then rubbed on the place of the seam area.

Rubbing the surface to be soldered with molten solder leads to a metallic bond between the solder and the surface and to removal of the oxide film from the surface.

The two existing methods of friction soldering differ by the method of abrasive removal of the oxide film from the surface of the parts to be soldered.

Removal of oxides occurs as a result of the mechanical abrading action of the solid particles included in the molten solder. In the first method of friction-soldering, the solid particles of solder (the solid phase) existing in the molten mass exert an abrasive action, whereas according to the second method, solid particles of foreign matter (asbestos, pumice stone, pile of brushes, etc.) deliberately incorporated in the molten mass, form an abrasive medium.

The first method of friction soldering has been used mainly in joining lead pipes (for water supply, etc.), for soldering of lead cable sheets and uniting the cable ends by special joints. In practice, the molten solder is poured in, and then the surface rubbed with molten solder by means of a wire brush, oakum, rags or leather. Abrasive action in removal of oxides is due to the solid particles present in the molten solder; consequently, this implies the use of low-melting solders with a wide range of the liquid-solid phase, i. e. a temperature range from the beginning of solidification (solidus) to the beginning of coalescence of freezing crystals. Of the low-melting tin-lead solders, most suitable for this purpose is an alloy containing 30% tin and having the largest crystallization range among the Sn-Pb alloys [1]; this solder retains its pasty form during soldering for a long time. In certain cases, the oxide skin can be removed by rubbing the surface with a soldering stick, heated over the temperature range between the solidus and the liquidus point.

A solder brought in the solid-liquid condition, i. e. heated over the effective crystallization range, may also be used for friction soldering: in this

* [Translator's note: the English term used is "friction-soldering"].

case, the crystalline skeleton acts as an oxide remover, while the liquid phase assists tinning.

Addition of a small amount of antimony to Pb-30% Sn solders improves their consistency and suitability for the friction soldering process. Friction soldering is done without a corrosive fluxing substance; sometimes wax or stearin are employed for protection only.

According to the German Standard of solders (DIN 1732), friction soldering may be carried out with the following zinc-bearing solders: 1) 85% Zn and 15% Al; 2) 60% Zn and 40% Sn; 3) 56% Zn and 44% Cd. These solders are used in joining cables and cast aluminum parts. Another suitable solder is the low-melting solder containing 60% Sn and 40% Zn. It is used in friction soldering of small joints and of foils up to 0.2 mm thick. A solder consisting of 90% Sn and 10% Zn is also used.

The crystallization range of a solder may be lowered by including in its mass some foreign abrasive particles forming a mechanical mixture with the solder.

Friction soldering is associated with pretinning of the surfaces. Pretinned parts unite if subjected to a certain pressure. If necessary, molten solder may be added and the parts preheated to the soldering temperature. During friction soldering, the molten solder has no independent motion as in capillary soldering, though capillary phenomena may also be present in friction soldering.

The friction soldering method is used in joining metal to glass by means of a eutectic indium-tin alloy (52 % In). For this to be done, the molten solder (with a melting point of 117°C), is applied by rubbing on the preheated surface of the glass object /2/. In this case, friction soldering is not connected with mechanical removal of oxides, but it assures only the bond between metal and glass.

For friction tinning, a simple procedure has been suggested, in which the low-melting solder is fused due to the heat of friction /3/. In practice, solder is applied by a slight pressure on a rotating abrasive disc, 6 mm in diameter and 12 mm in width. The rotating speed of the disc and the force of friction are chosen so that the solder melts during rubbing, and tightly adheres to the disc. If the disc is now brought in contact with the surface to be tinned, it is cleaned and at the same time friction-tinned with the solder, molten under the action of the abrasive disc. This procedure permits soldering of metal to glass, stainless steel to ceramics, or joining of titanium, molybdenum, tungsten, tantalum, or niobium. Prior to tinning, glass or ceramic surfaces should be preheated.

Solders used for this purpose should be low-melting and may have the following composition: 1) 40% Pb and 60% Sn; 2) 50% Pb and 50% Sn; 3) 50% Pb and 50% In; 4) 50% Sn and 50% In; 5) Wood's metal (quaternary eutectics of the Bi-Cd-Sn-Pb system).

Soldering may be done with a common soldering bit.

Sometimes, friction-soldering or tinning may be done with a solder brought to a pasty condition by heating. This helps in building up uneven surfaces in motor-car bodies, welded seams, etc. The soldering sticks preheated above their solidus point (i.e. to a pasty state) are often very brittle. When rubbed with coarse-grained solders, the surface becomes rough. To avoid this, fine-grained solders should be used. A fine-grain structure of tin solders may be obtained by adding arsenic /4/ or sulphur /5, 4/, to them while pouring into the ladle.

The use of fine-grained tin solders does not always help to avoid inter-crystalline brittleness of the solder layers due to slow crystallization of the solder. In such cases, the soldered seam is prone to become porous, and permeable to gas. Porosity of the tin-soldered seam may be eliminated by filling the seam with more fusible solders e.g. with an eutectic of 32% Pb, 15.5% Sn and 52.5% Bi, melting at 95°C. Filling of the porous seam is to be done right after friction soldering with low-melting solders; due to this procedure, the more fusible solder penetrates and fills the capillary pores of the seam.

Ya. M. Kanevskii suggested a fluxless method of tinning aluminum alloys by means of the so-called abrasive pencil. The technique involved is very simple, noiseless, and does not require any special equipment. Moreover, it allows tinning of very thin foil or wire.

The abrasive pencil is essentially a rod sintered from a mixture of soldering powder and ground asbestos. The optimal proportion of the components are: 10% (by weight) asbestos and 90% soldering alloy. The pencil is sintered in the press mold under a slight pressure (30–50 kg/cm²), which, due to the small diameter of the pencil (≤ 10 mm) may be achieved by clamping the rod in common locksmith vises.

The parts to be pretinned are preheated to a temperature exceeding by 25–50°C, the melting point of the solder involved, and then tinned by means of the abrasive stick by passing its end several times over the surface to be tinned. Usually, the thickness of the solder layer does not exceed 0.05 mm.

In order to increase the thickness of the soldered layer, the tinned surface is covered with small pieces of solder, which being molten, spread uniformly on the tinned surface.

Tinning may be hastened by heating the abrasive pencil in a special soldering lamp.

In soldering, the pretinned surfaces placed one above the other, are rubbed against each other to obtain a smooth thin seam, and then cooled. Tinning by means of the abrasive pencil may be done without any special preparation of the surface (i.e. by pickling, steel-brushing, emery cleaning, and degreasing). Aluminum alloys may be tinned without asbestos particles, by means of a low-melting solder having a wide crystallization range. In this case, the first grown solid crystals of the excess phase act as abrasive bodies which remove the oxide film. On the other hand, solders with a narrow range of crystallization and particularly eutectic solders are unable to remove the oxide skin from the surface to be soldered. The asbestos particles added to the molten solder, apparently play the role of abrasive agents. The abrasive pencil permits tinning of surfaces placed at any angle which, in other methods (e.g. in ultrasonic or low-frequency soldering) cannot be achieved. Another advantage of the abrasive pencil is an easy visual inspection of the work during soldering: non-tinned places of the surface appear as dull spots through the bright-lustrous tinned layer.

Friction soldering readily lends itself to automation. For this purpose various wire brush vibrating devices have been suggested. Among them, a tool manufactured by the firm Belard, is worthwhile; the wire brush of this tool vibrates in the molten solder with a frequency of 100 vibrations/sec. This tool is used in soldering aluminum parts. The tool requires solders composed of 80% Sn and 20% Zn. A solder containing 10% Zn assures a smoother surface of the soldered joint but is somewhat less corrosion resistant [6].

Further development of the friction welding methods (used mainly for rotating bodies) lead to a variety of the friction soldering method described above. In this alternative, a thin interlayer of solid low-melting solder is inserted between the closely located rotating parts; due to heating, as a result of friction between the rotating parts, the solder is molten, and forms the soldered joint upon cooling.

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CHAPTER XIV

ULTRASONIC SOLDERING

The tool, commercially known as an ultrasonic soldering bit, is essentially a device for fluxless tinning of the parts to be soldered. At present, the ultrasonic soldering bit is used for fluxless pretinning of aluminum and some of its alloys with low-melting solders.

Difficulties encountered in soldering aluminum and its alloys with low-melting solders, gave rise to the development of pretinning methods by means of ultrasonic soldering. Soldering with low-melting solders is applied for joining medium-loaded aluminum-alloy parts. The heating temperature of these parts is relatively low, thus preventing warping and distortion of the work during soldering, and maintaining sometimes high strength of the joint, acquired as a result of plastic deformation or heat-treatment (by hardening or aging). As known, heating parts at high temperatures in view of subsequent soldering is liable to cause considerable distortions (warping) of the soldered work. So, for instance, heating of cold-hardened aluminum alloys (commercial aluminum and the AMts alloy (1.6% Mn and the remainder Al), or of the Av alloy (0.4% Cu, 0.7% Mg, 0.25% Mn or Cr, and 0.8% Si) etc., causes softening. Duralumin, heated at a temperature above 250°C is also subjected to softening upon aging.

Pretinning of certain aluminum alloys by ultrasonic soldering methods, is based on the fact that the oxide film on the surface of the work is removed when molten solders are subjected to oscillations of ultrasonic frequency. This property was the basic principle in designing the first ultrasonic soldering tools, in the forties of the present century (the first patent rights for an ultrasonic soldering bit were granted in 1938-39) /1/, /2/. Two methods of soldering have been advanced: ultrasonic vibration of the soldering bit in molten solder and oscillation of the container filled with molten solder.

As shown /3/, oxide removal from the surface of aluminum alloys occurs as a result of cavitation processes, taking place under the effect of ultrasonic vibrations of the molten solder.

When ultrasonic vibrations of sufficient intensity are propagated in a fluid, longitudinal waves are formed. In the same place the fluid is alternately compressed and expanded as a result of the variable pressure of the ultrasonic waves. If the sound pressure changes by an amount equal to or higher than the atmospheric pressure, in the groups of waves that are in a negative phase, the pressure will be equal to zero or even below; this may lead to disruption of the fluid and to formation of bubbles.

These bubbles remain hollow or may be filled with gases dissolved in the fluid, or with vapor of the fluid proper. With a further increase of the pressure, the fluid bubbles start to clap and may even cause bursting. The increased pressure associated with clapping of the bubbles and considerable shifting of the fluid near the solid body immersed in it, has a destructive effect on the surface of the body (cavitation). So far, appearance of cavitation bubbles, their development and action on solid bodies has been little investigated. Interesting results have been obtained in investigating cavitation phenomena by ultrarapid photography /4/. Bubbles occur most easily in gas-saturated fluids, in the presence of solid particles or bodies. The cavitation properties of molten solders are still unknown. In the course of crystallization, cavitation may cause small blowholes in the solidifying (freezing) metal.

Destruction of metallic surfaces under the effect of cavitation phenomena has been thoroughly investigated /5/-/7/. Surface destructions of solid bodies due to cavitation phenomena have been noticed, particularly during the working of marine propellers or turbine blades. The oxide film covering the aluminum alloys is more easily destroyed than the base metal, and may be removed from the surface under the action of ultrasonic vibrations. Under definite conditions, especially at elevated temperatures (above 400°C), ultrasonic waves are able to remove not only the oxide film, but also particles of the base metal or alloy. Any increase in temperature leads to an increased cavitation destruction of the aluminum alloy. This imposes certain limits on the use of ultrasonic soldering tools. An efficient removal of oxide films due to cavitation phenomena in molten solder is possible only for a limited number of aluminum alloys; for instance, in high-magnesium aluminum alloys, ultrasonic vibrations are but little effective.

Ultrasonic treatment may be used in pretinning anode-coated aluminum alloys. For pretinning of small parts, it is sufficient to heat the solder and base metal with a soldering bit heated from a source of 50-100 w. Pretinning of large-sized parts implies additional heating in electric stoves or in furnaces.

Though the ultrasonic vibrations of the soldering tool, imparted to the molten solder, cause destruction of the oxide film formed on the surface of steel and copper, removal of such films is preferably done by more simple methods. Pretinning of beryllium, titanium, and their alloys, by means of the ultrasonic soldering bit proved not to be very efficient /8/, /9/.

Ultrasonic vibrations created in low-melting solders are liable to destroy thin wire or foils immersed in molten solder; therefore, pretinning of such parts proved to be impossible.

Ultrasonic vibrations with a frequency higher than 16 kc/s are inaudible to the human ear. Frequency of ultrasonic waves, used in pretinning operations does not exceed 25 kc/s. As it was found, reduction of frequency of ultrasonic vibrations, increases the intensity of the effect of cavitation /10/. This leads to the use of ultrasonic tools of a relatively low ultrasonic frequency.

Vibrations of 20-22 kc/s may be created by combining the soldering bit with an ultrasonic generator. The most popular method for generating sound-waves is the use of piezo-electric and magnetostrictive ultrasonic generators. The first type covers such crystals as quartz, Seignette salt, ammonium or potassium phosphates, barium titanate, etc, which are able to change their properties if exposed to an alternating magnetic field (the

inverse piezoelectric effect). The principle of the magnetostrictive generators (magnetostrictors) is based on the properties of ferro-magnetic metals (Ni and Co), of Invar (36% Ni and 64% Fe), monel metal (68% Ni and 32% Cu), permalloy (45% Ni and 55% Fe), permendur (50% Fe and 50% Co) and other alloys, to change their linear dimensions with the change of the magnetic field (Joule effect) /11/, /12/.

Most suitable for soldering purposes is the magnetostriction oscillator which, unlike the piezoelectric oscillator, may work at elevated temperatures. Nevertheless, the magnetostriction effect in metals and alloys decreases as heating proceeds, and completely disappears upon reaching the Curie point (800°C). By using permendur for magnetostriction oscillators, their working temperature may be increased up to 400°C /13/.

Figure 115 presents a schematic diagram of an ultrasonic soldering tool. A special valve oscillator transforms low-frequency current to a current of ultrasonic frequency, which, passing through the coil, creates an alternating electro-magnetic field. The magnetostrictor, placed inside the coil, under the action of this electromagnetic field starts to emit longitudinal ultrasonic vibrations.

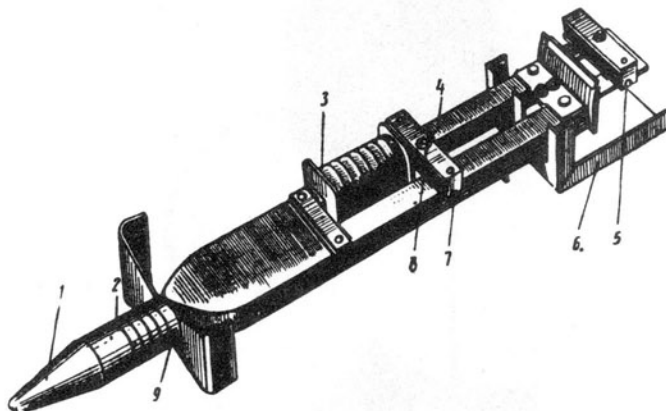


Figure 115. Diagrammatic representation of the ultrasonic soldering bit:

- 1—tool-bit; 2—heating element; 3—exciting coil;
- 4—magnetostrictor; 5—switch; 6—electric screen;
- 7—flexible insertions; 8—clamping; 9—membrane.

The ultrasonic soldering bit requires permanent magnetizing which may be achieved by mounting a permanent magnet parallel with the bit. One of the ends of the magnetostrictor is soldered to the vibrator bar (of a low-conductive alloy e.g. German silver); the length of this bar should be chosen so as to permit vibrating at the resonance frequency of the magnetostrictor. The bit of the soldering tool, made of monel metal, chrome-nickel steel or silver-nickel alloys, i.e. of alloys resisting cavitation in molten solders, is linked to the magnetostrictor through a membrane. Copper, though sometimes used for making bits, is unsuitable for ultrasonic tools, since it is liable to be destroyed under the action of cavitation and to be entrained into the joint. The bit is heated by means of a heating element (resister), through

which low voltage current is passing. To prevent overheating of the bit, the vibrator is sometimes fitted with cooling fins (see Figure 116).

Tinning of aluminum alloys is usually done in the following manner. The parts are thoroughly cleaned of dirt, paint, or grease; oxide films on the portions to be tinned are removed by customary mechanical or chemical methods. The work is then heated to a temperature slightly higher than the melting point of the solder; at the same time, the soldering bit is heated, and the previously cleaned bit is tinned by rapid dipping in molten solder. After switching the ultrasonic generator on, tinning of the work is accomplished by moving the soldering tool in the molten solder parallel to the surface to be tinned, without touching it with the bit. The molten solder may first be placed on the part in the form of droplets in which the bit of the ultrasonic tool is to be immersed.

The tinning rate with the ultrasonic tool varies within $0.16\text{--}0.25\text{ cm}^2/\text{sec}$.

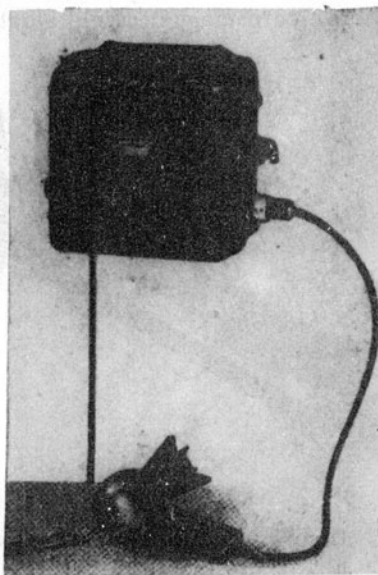


Figure 116. Siemens-Schuckert ultrasonic soldering bit, having cooling fins on the vibrator (connecting bar)

Prior to tinning with an ultrasonic soldering tool not fitted with a heating element, the parts should be heated up to the soldering temperature in an electric stove or furnace.

In using the ultrasonic soldering tool, removal of oxide films may be poorly done, thus leading to a poor quality of tinning. On portions still bearing traces of oxides left after removal, after a certain time the tinned coating is liable to exfoliate, and on the places of exfoliation, formation of peculiar bubbles may be noticed. The quality of tinning may be checked by a simple method: if a rag is passed over the surface covered with molten solder, the poorly tinned portions of the work will remain unsoldered and should therefore be subjected to retinning.

Usually, oxides on the edges of a tinned part are persistent and therefore, the tinned layer after a certain time, is liable to peel from such portions.

At present, ultrasonic soldering tools of various design are manufactured by different firms, e.g. the tools offered by the firms Mullard /14/, and Siemens-Schuckert /15, 16/. The ultrasonic soldering tools produced in the USSR are known under the trademark of UP-21 soldering tools (Figure 117). Table 80 presents some technical characteristics of these tools.

Technical characteristics of the UP-21 ultrasonic soldering bit and the UP-31 ultrasonic soldering bath Table 80

	Type of unit	
	UP-21	UP-31
Working frequency	18-22	18-22
Generator output, in w	40	250
Overall dimensions in mm, of:		
generator	332 × 342 × 310	450 × 305 × 280
soldering bit	292 × 160 × 52	—
support	205 × 105 × 138	—
soldering bath	288 × 200 × 162	245 × 350 × 370
Diameter of the bath, mm	25	100 × 100
Depth of the bath, mm	10	25
Weight in kg of:		
generator	14	20
soldering bit	1.1	—
support	0.25	—
bath	0.8	28

Thin wire, foils, or small-sized parts may be tinned by dipping in a bath of molten solder, connected to the magnetostrictor of the ultrasonic tool, the soldering bit of which has been previously removed. The bath may vary in shape but its sizes are limited by the output of the high-frequency oscillator. Parts which should not be tinned on their whole surface, are subjected to anode or phosphate coating prior to tinning in the ultrasonic soldering bath, and the portions to be tinned are cleaned mechanically of the oxide skin. After heating to the melting point of the solder, the work to be tinned is immersed in the molten bath previously connected to the source of ultrasonic vibrations. The time cycle of tinning depends upon size and shape of the work, usually varying from 5 to 40 sec. Tinning in the ultrasonic bath is more efficient and yields a higher quality of the soldered seam than tinning with an ultrasonic tool.

Table 80 presents features of the UP-31 ultrasonic tinning bath fabricated in the Soviet Union.

Ultrasonic tinning of aluminum alloys may be also achieved by plunging the parts and the tip of the ultrasonic tool in molten solder. The tip of the tool, moving along the surface of the work, carries out the tinning. So far this method has been used only in few applications.

After tinning by means of ultrasonic vibrations, the parts are assembled in view of their subsequent soldering, and then heated to a temperature ex-

ceeding the liquidus of the solder by 30–50°C. After heating, soldering is carried out by means of a solder stick or an electric soldering bit /17/-/23/.

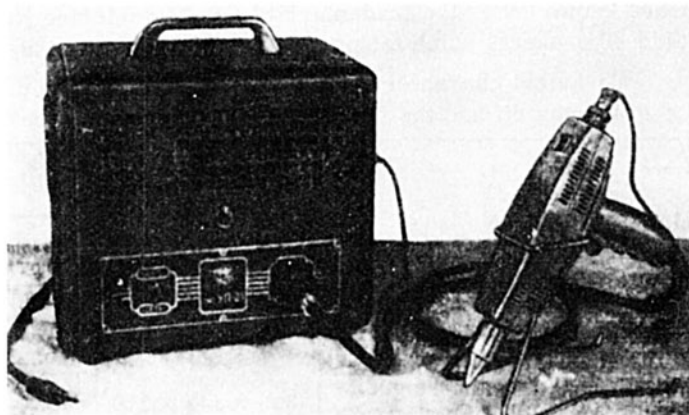


Figure 117. The UP-21 ultrasonic soldering bit and its generator

Oxide coatings on the surface of aluminum alloys may be most efficiently removed through cavitation caused by low frequency vibrations. For this purpose, Ya.M. Kanevskii and N.T. Sharygin suggested soldering tools with electromechanical and pneumatic vibrators.

An essential disadvantage of low-frequency vibrators is the poor tinning of the surface in using solders of a eutectic composition, and noise during operation.

Intrasonic soldering using various low-melting soldering alloys may be used. Due to a better corrosion resistance, usually tin-zinc solders (80% Sn and 20% Zn) are employed.

Soldering by means of ultrasonic tools or baths may be done also with different solders of the Zn–Sn, or Zn–Sn–Cd systems with or without addition of silver. Aluminum joints made with solders of the following composition: 1) 20–30% Zn, 1–2% Ag, and the remainder, Sn, melting at 260–280°C; 2) 40–44% Zn, 2–3% Ag, and the remainder Sn, melting at 320–350°C, exhibit satisfactory properties when exposed to open air or introduced in a damp chamber, sprinkled with fresh (drinking) water. Addition of silver increases the corrosion resistance of the solder and the strength of the soldered seam. Joints made with solders of the P300A-type (see Chapter V) tend to undergo overall corrosion in a tropical climate.

Soldering with P200 or P250 solders implies a careful inspection of the tinned surface, the more so as tinning by means of such solders is carried out at relatively low temperatures, and diffusion processes which lead to a bond between the solder and the base metal, develop slower than in soldering with less fusible solders.

For the time being, ultrasonic soldering of titanium and magnesium, did not yield any satisfactory results.

Soldering bits for fluxless soldering, based on the cavitation destruction of the oxide film have the following disadvantages:

- 1) Complicated construction of the electronic equipment used in ultrasonic soldering.
- 2) Rapid wear of certain parts of the pneumatic low-frequency soldering bits during operation.

3) Rapid fatigue of the operator during soldering with low-frequency soldering tools due to the intense noise in working.

4) Impossibility of tinplating foils and very thin wire, as they are subjected to the action of cavitation during the tinning process.

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Chapter XV

SOLDERING IN GASEOUS ATMOSPHERES

Soldering of parts in contact with or integrally surrounded by a special gaseous atmosphere is termed gas soldering.

The gaseous atmosphere (like the fluid one) while in direct contact with the parts to be soldered, may either be chemically inert, protecting the parts from atmospheric corrosion, or chemically active, favoring decomposition and removal of the solid (particular oxide) coating from the surface of the parts to be soldered.

Flux-covered gas soldering is essentially a combined method, in which the fluid medium (the flux) constitutes an intermediate active medium between the work and the gaseous atmosphere.

Another combined method, apart from open air-soldering or flux-covered soldering in air furnaces, is soldering with gas-forming liquid fluxes which create a local gaseous atmosphere protecting the parts to be soldered from contact with the active elements of the air. Unlike welding with gas-forming fluxes, this soldering method is so far still in the process of study.

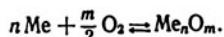
§ 1. Principles of Soldering in a Gaseous Atmosphere with a Reduced Partial Pressure of Oxygen

During soldering, the chemical activity of the gaseous atmosphere may foster decay and removal of the solid film (particularly oxides) from the surface of the parts to be soldered, by decomposing this film in its components or by combining the elements of the solid film (particularly the oxygen) with easily removable compounds.

The solid surface film of the parts to be soldered, may be formed by sulphides, borides, phosphides, oxides, and other, usually inorganic substances which depend on the gaseous atmosphere. Further in this study only oxides formed in an oxidizing gaseous medium will be considered.

Soldering of metals and alloys is connected with separation of oxygen ions from the metallic ions present in oxides. Such separation depends upon the strength of the chemical bond between the oxygen ions and the metal involved. This bond may be estimated in different ways; to a rough approximation it may be determined by the heat of formation (ΔH), and still

more accurately by the change in free energy (ΔF), or by the maximum work obtainable from the chemical reaction



Thermodynamic calculations contain many constants which cannot be determined by experiment, and therefore arbitrarily they are given a definite magnitude. This refers particularly to elements in a state of equilibrium at 25°C, the enthalpy of which is said to be equal to zero; the heat of formation of oxides is related to the absolute temperature 2980C (ΔH_{298}). Heat of formation may be conveniently expressed with respect to 1 mole of oxygen (O_2). Table 81 presents some data on the heat of formation for a series of oxides /1/, /2/.

As shown in Table 81, metals like gold, silver, or palladium, do not form stable oxides, and therefore their oxide films may be relatively easily destroyed. Higher on the stability scale are to be found copper, lead or cadmium oxides. Cobalt, iron, nickel, tin, tungsten, molybdenum, or manganese oxides have nearly the same stability. Manganese has a stronger bond with oxygen than the ferrous metals. The stability of zinc oxides approaches that of manganese oxides.

Still higher on the stability scale may be found the oxides of chromium, tantalum, vanadium, titanium, boron, zirconium, aluminum, or beryllium. Beryllium oxides have much higher stability than many other metals.

Metals and their alloys, may be classified according to the difficulties in soldering. They may be classified in groups according to the increase in the heat of formation (or dissociation) from oxides, i. e. in groups according to the difficulty of separation of oxygen ions from the metallic ions.

Soldering of noble metals does not present any special difficulties. More difficult to solder are copper, lead, or cadmium. Ferrous metals lend themselves with more difficulty to soldering than does copper. Tungsten and molybdenum are closely related to the ferrous group with respect to their difficulty in soldering. Zinc and manganese present more difficulties in soldering than do ferrous metals. Still more difficult to solder are chromium, titanium, zirconium, aluminum, magnesium, or beryllium.

In considering the strength of the chemical bond between the oxides and the base metal, two circumstances have to be taken into account. Certain metals are prone to form different oxides of varying stability, and therefore difficulties in their soldering are determined by the kind of oxides formed on such metals.

As a rule oxides formed on the surface of multicomponent alloys, are not pure metallic but solid solutions of oxides.

MnO , FeO , NiO , CoO , and a series of other oxides of the same type (MeO), the oxides Fe_2O_3 , Cr_2O_3 , Al_2O_3 (Me_2O_3), and the spinel type oxides Fe_3O_4 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, $\text{NiO}\cdot\text{Cr}_2\text{O}_3$, etc ($\text{MeO}\cdot\text{Me}_2\text{O}_3$) have an isomorphous structure and are liable to form among themselves solid solutions.

The heat of formation of oxides on the surface of metals may be smaller or larger than in the case of oxides formed on alloys of the same metals. Accordingly, soldering of alloys may either be easier or more difficult than soldering pure metals.

At present, no reliable data about the effect of the alloying components

Table 81

Heat of formation of certain oxides (ΔH_{298})

Type of oxides	Reaction of formation of oxides	Heat of formation of 1 mole oxide, kcal	Heat of formation of oxides, related to 1 mole O_2 ; in kcal
Au_2O_3	$2Au + \frac{3}{2}O_2$	-11	-7.3
Ag_2O	$2Ag + \frac{1}{2}O_2$	7.3	14.6
PdO	$Pd + \frac{1}{2}O_2$	21.0	42.0
PbO	$Pb + \frac{1}{2}O_2$	52.0	104
PbO_2	$Pb + O_2$	65.0	65.0
CuO	$Cu_2O + \frac{1}{2}O_2$	37.5	75.0
Cu_2O	$2Cu + \frac{1}{2}O_2$	41.0	82
CoO	$Co + \frac{1}{2}O_2$	57.5	115.0
Co_3O_4	$3Co + 2O_2$	196.5	98.2
H_2O (liquid)	$2H + \frac{1}{2}O_2$	57.8	115.6
H_2O (gaseous)	$2H + \frac{1}{2}O_2$	68.3	136.6
NiO	$Ni + \frac{1}{2}O_2$	58.4	116.8
CdO	$Cd + \frac{1}{2}O_2$	62.2	124.4
FeO	$Fe + \frac{1}{2}O_2$	64.5	129.0
Fe_2O_3	$2Fe + \frac{3}{2}O_2$	195.2	130.0
Fe_3O_4	$3Fe + 2O_2$	266.8	133.8
MoO_2	$Mo + O_2$	130.0	130.0
MoO_3	$Mo + \frac{3}{2}O_2$	180.5	120.3
WO_2	$W + O_2$	134.5	134.5
WO_3	$W + \frac{3}{2}O_2$	200.0	133.3
W_2O_5	$2W + \frac{5}{2}O_2$	335.0	134.0
SnO_2	$Sn + O_2$	138.1	138.1
Mn_2O_3	$2Mn + \frac{3}{2}O_2$	232.5	151.6
Mn_2O_4	$3Mn + 2O_2$	332.0	161.0
MnO	$Mn + \frac{1}{2}O_2$	92.5	185.0
ZnO	$Zn + \frac{1}{2}O_2$	83.4	166.8
Cr_2O_3	$2Cr + \frac{3}{2}O_2$	269.5	179.6
NbO_2	$Nb + O_2$	193.5	193.5
Nb_2O_5	$2Nb + \frac{5}{2}O_2$	463.0	185.2
Ta_2O_5	$2Ta + \frac{5}{2}O_2$	499.0	199.6
V_2O_3	$2V + \frac{3}{2}O_2$	300.0	200.0
SiO_2	$Si + O_2$	208.3	208.3
TiO_2	$Ti + O_2$	219.0	219.0
B_2O_2	$2B + \frac{3}{2}O_2$	345.0	230.0
ZrO_2	$Zr + O_2$	258.5	258.5
Al_2O_3	$2Al + \frac{3}{2}O_2$	400.0	266.6
MgO	$Mg + \frac{1}{2}O_2$	144.0	288.0
BeO	$Be + \frac{1}{2}O_2$	147.3	294.6

on the strength of their oxides, are available. In the light of this fact, some cases of relatively easy soldering of multicomponent alloys or steels, become explicable; on the other hand, difficulties in soldering certain chrome steels are often exaggerated, since it is usually admitted that Cr_2O_3 forms with them a strong bond; actually together with these oxides, other oxides may be encountered $(\text{Fe}, \text{Cr})_2\text{O}_3$, the bond of which is weaker than in the Cr_2O_3 oxide. During oxidation, the surface of many alloys is covered with an oxide film of non-uniform chemical composition, sometimes consisting of several layers of different oxides (depending on temperature and duration of the oxidation process). These facts complicate the theoretical study of the soldering of metals and alloys.

Changes of free energy, ΔF , as a function of temperature over a certain range, are given by:

$$\Delta F = -A - B \log T + CT$$

or with sufficient accuracy, by:

$$\Delta F = -A + BT$$

Here, A, B, C, are constants, and T is the absolute temperature.

Variation of the linear law of free energy may occur at the temperature of the change of state. Theoretical data on the variation of free energy during formation of oxides may be found in the literature survey [1/-/3/].

The Diagram in Figure 118 presents data on the temperature dependence of the free energy of certain oxides. On this chart the variation of free energy has been related to 1 mole of oxygen, combined with the corresponding quantity of metals in the oxides at a pressure of the gaseous medium equal to 1 atm.

The angular coefficient of variation of free energy equals the change of entropy, Δs given by

$$\Delta F = \Delta H - T\Delta s$$

where ΔF = variation of free energy; ΔH = heat effect of reaction; T = absolute temperature, and Δs = variation of entropy.

With the increase in temperature, variation of free energy, connected with formation of oxides, decreases. Consequently, destruction of oxides is easier to accomplish at higher temperatures. Starting from a definite temperature typical of every oxide, decomposition of oxides in elements occurs spontaneously (dissociation of oxides). The temperature of spontaneous dissociation of oxides depends in principle, upon the partial pressure of the oxygen in the surrounding medium.

In a common environment, in which the partial pressure of oxygen equals 0.21 atm, carrying out fluxless soldering is quite impossible for most commercially known metals and alloys, since the temperature of dissociation of their oxides, largely exceeds their melting point. Platinum, silver, gold and their alloys, are exceptions, since their oxides tend to dissociate at temperatures below the melting point of the corresponding metal.

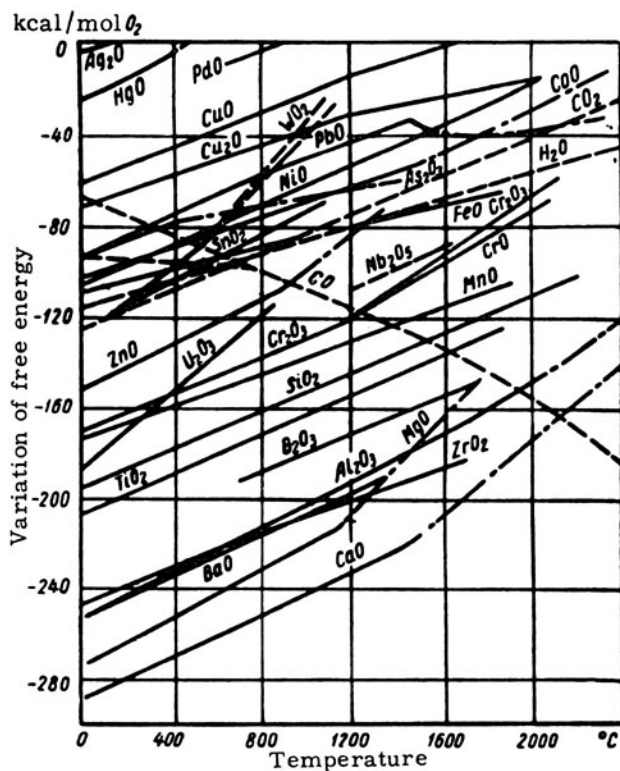


Figure 118. Variation of free energy of oxides /8/

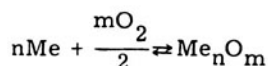
In the following, temperatures at which the partial pressure of dissociation of oxides becomes equal to 0.21 atm /4/, are given:

Oxide	PtO ₂	Ag ₂ O	Au ₂ O	CdO	Cu ₂ O	PbO	NiO	FeO	MnO
Absolute Tempera- ture (°K)	300	250	300	900	1935	2348	2751	3000	3500

A decrease in the partial pressure of oxygen in the surrounding medium, favors spontaneous decomposition of oxides, and hence, soldering of metals and alloys.

The study of the effect of the surrounding medium on spontaneous decomposition of oxides may be facilitated by using the relationship between variation of free energy and the constant of equilibrium /1/, /3/-/6/.

The equilibrium constant of a reversible reaction,



can be written

$$K'_p = \frac{p_{\text{Me}}^n \cdot p_{\text{O}_2}^{\frac{m}{2}}}{p_{\text{Me}_n\text{O}_m}}$$

where p_{Me} , p_{O_2} , and $p_{\text{Me}_n\text{O}_m}$ = partial vapor pressure of metal, oxygen and oxides, in atm.

The chemical components of the reaction, being in a state of condensation have constant values; therefore, if oxygen is the single gas which takes part in the reaction, one may write

$$K_p = p_{\text{O}_2}$$

where p_{O_2} = partial pressure of oxygen.

Variation of free energy during formation of oxides, in cases where the partial vapor pressures of all the gaseous components is originally equal to the unit, is given by

$$\Delta F = -RT \ln K_p = -4.576 T \log p_{\text{O}_2}$$

where R = universal gas constant; T = absolute temperature; K_p = equilibrium constant.

The partial vapor pressure of an oxide reflects the degree of its stability: the smaller the pressure, the stronger the bond between the oxide and the base metal.

Formation and decay of an oxide depend upon the condition of the surrounding medium, and particularly on the partial pressure of the oxygen present in this medium. If the partial vapor pressure of oxides at a given temperature is less than the partial pressure of oxygen in the surrounding gaseous medium, oxidation of the metal will occur; on the other hand, if the partial pressure of oxygen is less than the partial vapor pressure of the oxides, their decay and reduction of the metal will take place.

The dissociation pressure of an oxide may be found by means of one of the Nernst formulae. The simplified Nernst formula is

$$\lg K_p = -\frac{\Delta H}{4.574 T} + \Sigma \nu 1.75 \lg T + \Sigma (n_i),$$

where ΔH = heat of formation of oxides at 298°; $\Sigma \nu$ = algebraic sum of the number of gas molecules in both the left and right members of the equation; $\Sigma(n_i)$ = algebraic sum of the product of multiplying the conventional chemical Nernst constants by the number of the corresponding gas molecules of the given substance taking part in the reaction.

The dissociation pressure increases with the increase in temperature. In a given gaseous atmosphere (at a given partial pressure of oxygen), the oxide starts to decompose spontaneously when temperature reaches a definite value.

As may be seen from the above, decomposition of oxides may be accomplished by increasing the temperature and reduction of the partial pressure of the oxygen from the gaseous surrounding medium. In order to control these processes, one must know the dissociation pressure of the different oxides, and its variation with the temperature. Figure 119 presents data on the variation of the dissociation pressure of a series of oxides, with the temperature /7/.

Only oxides of noble metals possess a rather high dissociation pressure; they may decompose at relatively low temperatures and at a considerable partial pressure of the oxygen in the surrounding medium. Other oxides require for their decay elevated temperatures and a low partial pressure of oxygen in the gaseous medium.

The diagram (Figure 119) representing variation of the dissociation pressure of oxides may be helpful in selecting conditions for fluxless soldering of metals upon which a certain oxide forms /8/: 1) the whole area of temperatures and partial pressures of oxygen below the line of reaction equilibrium, corresponds to the conditions of a possible spontaneous decay of oxides; 2) the areas of temperature and partial pressure of oxygen above this line correspond to the condition of oxidation of the metal.

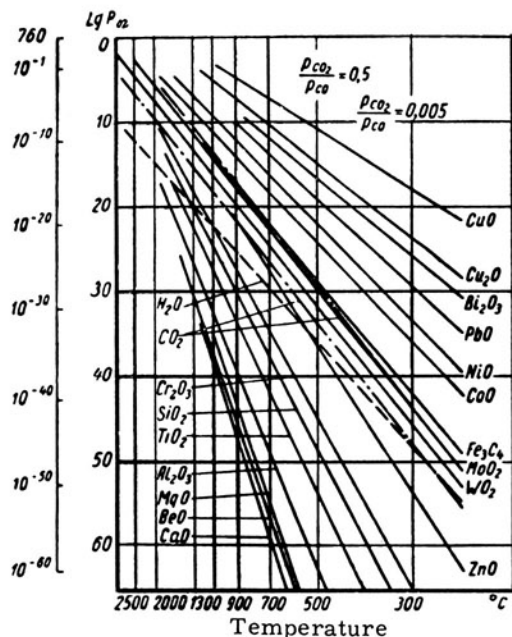


Figure 119. Variation of dissociation pressure of oxides /7/

Considerable reduction of the partial pressure of oxygen from the gaseous atmosphere, may be achieved in two ways: by formation of a vacuum with a definite rarefaction of the air, and by filling the surrounding space of the parts to be soldered with inert gases. In the first instance, variation of partial pressure of oxygen occurs without altering the composition of the gaseous atmosphere whereas in the second case, its composition is changed

Of great importance for the soldering process is the process of evaporation of metals and oxides during heating before soldering, and particularly during vacuum heating. Evaporation of metals increases with the increase in temperature and with the degree of rarefaction of the surrounding air.

Table 82 contains some data on the temperature of visible evaporation of certain metals in a vacuum with a residual pressure of 10^{-1} and 10^{-2} mm of mercury. As can be seen, elements like Zn, Cd, Cr, Mn or Si undergo a marked evaporation during vacuum soldering.

Table 82

Temperature of visible evaporation of certain elements in vacuum /9/, /10/.

Element	Melting point, °C	Visible evaporation at °C		Element	Melting point, °C	Visible evaporation at °C	
		10 ⁻² mm mercury	10 ⁻¹ mm mercury			10 ⁻² mm mercury	10 ⁻¹ mm mercury
Cu	1033	946	1035	Sn	232	823	922
Ag	961	767	848	Pb	328	483	548
Be	1284	942	1029	V	1697	1465	1586
Mg	651	287	331	Nb	2500	2194	2355
Zn	419	211	248	Ta	2996	2407	2599
Cd	321	148	180	Sb	630	466	525
B	2000	1052	1140	Cr	1900	907	992
Al	660	724	808	Mo	2622	1923	2090
In	157	667	746	W	3382	2554	2767
Th	304	405	461	Mn	1244	717	791
C	3214	2129	2288	Fe	1535	1094	1195
Si	1410	1024	1116	Co	1478	1249	1362
Ti	1965	1134	1249	Ni	1455	1157	1257
Zr	2127	1527	1660	Pd	1555	1156	1271
				Pt	1774	1606	1744

At a higher vacuum ($\sim 10^{-4}$ mm of mercury), particularly at a temperature of 1000°C, most metals exhibit visible evaporation (volatilization).

In case of vacuum evaporation of the alloying elements, in the first approximation Raoult's law (as applicable to diluted solutions) may be considered valid; according to this law, the vapor pressure in a solution is smaller than the vapor pressure of the pure solvent by an amount proportional to the concentration of the dissolved substance /9/.

Certain metallic oxides have an appreciable vapor pressure when evaporated in a relatively low vacuum. So, for instance, in a vacuum with a residual pressure of 10^{-5} mm of mercury, the oxides CaO, SrO, BaO, V₂O₅ and MoO₂ are liable to evaporate over a temperature range from 1000 to 1200°C; Cr₂O₃ evaporates at 1900°C; NiO, at 1070°C; MoO₃, at 600°C, and WO₂ at 800°C /8/, /11/, /12/. The oxide Al₂O₃ exhibits in this connection an extreme stability. Its vapor pressure is so low, that

visible evaporation takes place only at a temperature close to the melting point of that oxide (2050°C). On the other hand, oxides of Be, Mg, Si, Zr, or Cr, heated in a vacuum varying from 10^{-3} to 10^{-5} mm of mercury, exhibit a visible evaporation over a temperature range from 1600 to 2000°C.

§ 2. Vacuum Soldering

Vacuum soldering of metals achieved through furnace heating may be accomplished according to one of the following two systems.

1) Soldering in furnaces the heating chamber of which is previously rarefied (fixed heating chamber). The merit of furnaces with fixed heating chambers lies in the possibility of assuring a high and stable vacuum with a residual pressure from $1 \cdot 10^{-5}$ to 10^{-6} mm of mercury. Soldering in such furnaces requires high costs in equipment and maintenance. Their disadvantage lies in the extremely slow cooling rate of the soldered part (for several hours) due to the reduced heat conductivity of the rarefied heating chamber [12/, 13/]. In many alloys, such a prolonged heating time at elevated temperatures leads to an intense growth of the crystalline grain, and to a large deterioration of the mechanical and other properties of the soldered joint.

2) Vacuum soldering by separating the vacuum chamber from the heating space. Such a unit consists of a heating furnace and a vacuum chamber inserted in the furnace. The vacuum chamber is evacuated at room temperature; the chamber then is introduced into the furnace where the temperature is raised to the soldering temperature, while the pumping out of air from the vacuum chamber is not interrupted.

Withdrawal of the vacuum container from the furnace after completion of soldering permits rapid cooling of the work. A single heating furnace may be used for successive heating of several containers properly prepared for soldering [14/].

Heating of the parts prior to vacuum soldering may be done in electric resistance furnaces or in high-frequency induction units. In the first case, furnaces with nichrome heating elements (for temperatures up to 1100°C) are used; soldering at higher temperatures is done in furnaces having molybdenum or ceramic heating elements. Molybdenum heating elements are particularly prone to oxidation at temperatures above 400°C; therefore, prior to putting such a furnace into operation, the air from the vacuum chamber is pumped out and then the molybdenum heating element is switched in. For the same reason, after soldering, air for cooling of the work may be admitted into the vacuum chamber only if its temperature is below 400°C.

In induction-heated steel or graphite-muffle furnaces, heating and cooling of the soldered parts occurs much faster than in electric-resistance furnaces. In these units, heat is transmitted by radiation from the muffle walls externally heated in the electromagnetic field of the inductor coil.

In soldering according to the second system, heating is achieved in electric-resistance furnaces or in electric furnaces with nichrome, selite, or carborundum heating elements. In this case, induction-heating may also be used. If the parts to be soldered are heated by high-frequency currents, the heating chamber may be made of molybdenum or of pyrex glass.

The vacuum soldering unit for high-frequency heating, first devised by V. N. Vologdin /15/, consisted of a copper table with a polished plate covered with a glass hood, whose polished edges were smeared with technical vaseline to assure a tight adherence to the table plate. The air from inside the glass hood was pumped out through a pipe mounted in the table plate, and connected to the vacuum pump. The work placed under the glass hood after bringing the vacuum to a pressure of 10^{-3} mm of mercury, was heated by means of a high-frequency inductor coil mounted outside of the glass hood. Owing to the low heat-conductivity of the vacuum space, cooling of the work occurred much slower than after heating in air. In order to prevent oxidation of the surface of the parts to be soldered, air for cooling the work was admitted into the glass hood at a temperature no higher than 100-150°C.

Vacuum soldering combined with high-frequency heating has little use, due to low efficiency, difficult maintenance of the equipment, and the limited possible use, e. g. to solder only small-sized parts having the geometrical shape of rotating bodies. In order to increase efficiency of the vacuum soldering process, automatic units of the rotary table type are sometimes used, in which a rotating table is provided with several hoods placed on the circumference of the table and connected to a vacuum pump. The table is of the intermittent-motion type. After placing the hood on the inductor coil, the latter lowers and heats the work. After raising the work to the requisite temperature, the inductor coil is cut off and raised; the table is given a new turn to bring to the inductor coil the next hood with the parts to be heated. This method is applied for soldering of spark plugs of internal combustion engines.

Welded heating-containers for vacuum soldering are made of low-carbon, stainless, or heat-resistant steel (of the 10, 20, or 1X18N9T, EI654 grades, etc), and consist of a chamber for the work to be soldered, and a pipe for connection to the vacuum pump. The temperature inside the container is measured by means of a glass-bead insulated thermocouple, the junctions of which are connected to rigid molybdenum conductors soldered to the glass hood; these conductors are inserted through the vacuum pipe. The thermocouple may be inserted into the container also through a special connecting pipe, welded to the container prior to introducing the work to be soldered, in order to prevent heating and oxidation of the work. In sealing up the container, much attention must be paid to avoid intense heating and thus oxidation of the work placed inside the container.

For this purpose, that part of the container most distant from the work is first welded; alternately seam or spot-welding may also be applied (with overlapping of the nuggets).

When soldering is done in a vacuum container, clamping of the parts to be soldered is better made through a pressure difference between the inner and outer walls of the container. In this case, the wall to which the work should be pressed, is made of thin steel sheet, 0.6-1.0 mm thick. In evacuating the air from the container, the work will be pressed against the thin steel walls. For soldering of irregularly shaped parts, the steel container is properly shaped to fit the form of the work to be soldered; alternately, the space between the work and walls may be filled with heat resistant granulated corundum (grain size, 2-3 mm), through which pressure from the wall to the parts is transmitted.

The type of vacuum pump required for evacuation of the air from the

soldering container is chosen according to the volume of the container and the maximum vacuum required by the soldering process.

For low-vacuum soldering with small containers, mechanical vacuum pumps of the following type may be used: the RVN-20 rotary pump (of the rotating blade type), the VN-1 piston (plunger) pump, etc. For high temperature soldering, vacuum down to 10^{-3} millimeters of mercury is obtained in two stages: preliminary evacuation of air down to a residual pressure of $3 \cdot 5 \cdot 10^{-3}$ mm of mercury is done by means of the VN-2 or RVN-20 mechanical pumps; a metallic high-vacuum (diffusion-type) pump (e.g. the N-2T or N-5S type) completes the rarefaction cycle.

For vacuum soldering in induction-heated muffle furnaces, booster-type vacuum pumps (e.g. of the BN-3 type) are used.

Special filters mounted in the vacuum piping between pump and container, protect the pumping unit from being clogged with foreign (mechanical) matter.

Gas pressure in the vacuum system is measured by means of vacuum meters. A residual pressure down to 1 mm of mercury is measured with the Bourdon type (spring coil) vacuum gage; higher vacuum (down to 10^{-3} mm of mercury) may be measured by means of the cold-cathode ionization vacuum gage, the thermocouple vacuum gage with bimetallic screen, etc. A still greater vacuum can be measured with the hot-cathode type ionization gauge, the compression vacuum gage or the radiometer vacuum gage /16/.

Soldering of metals in vacuum-soldering units often is associated with removal of oxides, grease, oil, dirt, or gases; therefore, a thorough cleaning of the surfaces, preparatory to soldering may not always be necessary.

The vacuum soldering process usually may be divided into the following stages:

- 1) The work ready assembled for soldering, is placed in the container. Special shims are used to prevent welding of the work to the container walls. Asbestos or slate asbestos is less suitable as a material for shims in vacuum or in an argon atmosphere, due to evolution of gases during heating. Insulating shims may be made more conveniently of mica, spongy refractory clay, graphite, or oxide coated titanium or stainless steel.

- 2) The container is then seal-welded and tested for air-tightness by immersing in water, and by blowing compressed air through the vacuum pipe, under a pressure of 4-5 atm. Leakages are removed by building up where necessary until complete tightness is achieved.

- 3) The container is then connected through a filter with the preliminary vacuum pump which draws the air from the container at 20°C . Afterwards if necessary, the diffusion type vacuum pump may be connected to obtain a higher vacuum.

- 4) The container prepared in this way is put in the furnace, without interrupting the air evacuation process: preheating of the container is associated with lowering of the vacuum due to gases evolved from the work, the solder, and the walls of the container, and also due to air-infiltrations through leakages in the system. Due to these factors, the vacuum in the container should be restored after a certain time.

Soldering of copper and nickel may be done successfully at a relatively small vacuum (of $\sim 10^{-1}$ to $5 \cdot 10^{-2}$ mm of mercury). On the other hand, a residual pressure of 10^{-3} mm of mercury is insufficient for soldering stainless steels and heat-resistant or thermostable nickel alloys of the

EI437 type, since during soldering their surface is liable to be covered with chromium oxides or with chromium-containing iron oxides. In such cases, a small amount of fluxing substances should be used. This may be done by boiling the ready assembled work prior to soldering in an aqueous solution of a fluxing agent (e.g. the 200-grade flux) for 15-25 min. After drying at 100-120°C for 20-30 min, the parts may be subjected to vacuum soldering. The fluxing agent may be used also in the form of a low-consistency paste applied in a thin layer. During high-temperature soldering, a great part of the fluxing substance (e.g. the 200 type flux) tends to evaporate.

Thin-walled steel parts, when soldered in the vacuum container at high temperatures, are prone to be squeezed by the pressure of the container walls. In such cases, the vacuum in the container should not exceed a minimum value necessary for clamping the work to the wall.

An appreciable reduction of the partial pressure of oxygen present in the container, may be obtained by continuous pumping out of the air and replacing it by argon gas which assures clamping of the work.

This method is applied e.g. for soldering of stainless-steel honeycomb structures /17/.

Soldering of stainless steel parts according to the method stated above, essentially occurs in a stagnant argon-gas medium, and may be carried out successfully only if the surface of the work is covered with a thin copper or flux layer.

Soldering of internal components can be done after welding of the work and evacuation of the air through a special connection pipe welded onto the work. In such cases a special container for protecting the work from direct heating may be used; to prevent oxidation of the outer surface of the work, the container should be filled with an inert gas (argon or nitrogen).

Vacuum soldering of nickel, copper base alloys, or stainless steel yields (by ~ 50 %) stronger joints than soldering in a hydrogen atmosphere /18/. Soldering of nimonic-90 or nimonic-100 alloys with nickel-base solders containing a large amount of Cr or Mn, can be done successfully only at a maximum residual pressure of 10^{-5} mm of mercury. If soldering at a lower vacuum, fluxes should be used.

Vacuum soldering is used for metal coating of glass and ceramics, for metal joining of synthetic sapphire, carbides, graphite etc. This method is based on the fact that hydrides of Ti, Zr, or Nb dissociate when heated up to a certain temperature, forming on the surface of the part to be soldered a layer of pure metal contained in the hydride. Ti and Nb are extremely susceptible even to small quantities of oxygen, and therefore soldering with hydrides of such metals is to be done at a certain vacuum (10^{-4} mm of mercury) or in an atmosphere of inert gases /18/. For soldering with zirconium hydrides, a dry nitrogen atmosphere may be used. Metallic hydrides (prepared in water or nitrocellulose) may be applied also in the form of a paste to coat the surface of the material to be soldered. For this to be done, the work is previously assembled and then coated with the pre-soldering paste. While heated in vacuum at the temperature of dissociation of the hydrides, which should be below the melting point of the solder, the surface of the work is coated with a thin layer of pure metal, Ti, Zr, Ta and Nb resulted from reduction of the metallic hydride. On this interlayer, the molten solder can spread easily.

This interlayer soldering-method may be used also in soldering of

aluminum alloys; since aluminum alloys cannot be soldered in a hydrogen atmosphere, niobium or titanium hydrides may be used most successfully for this purpose.

Vacuum soldering may be employed in joining tungsten or molybdenum parts with solders of the high-melting (above 2,200°C) armco-iron type, and in soldering high-melting metals (Mo, W, etc) to graphite parts. Carbides of these metals form during soldering intermediate layers between the parts to be soldered./19/. Vacuum soldering of nickel or copper-coated stainless parts (residual pressure 10^{-2} to $5 \cdot 10^{-2}$ mm of mercury) requires brass solders (of the L62, L62N, or other types), and/or tin and nickel-manganese bronzes containing a certain amount of silicon.

§ 3. Soldering in an Atmosphere of Inert Gases

Usually, soldering in an atmosphere of inert gases is done in special containers, though in certain cases, muffle type furnaces may also be useful, the muffle being filled with an inert gas (e.g. argon or helium).

When argon is introduced into the container under a definite pressure, a certain amount of oxygen is displaced together with the air, and the partial pressure of the remaining oxygen becomes smaller than in the mixture with air. The partial pressure of oxygen can be reduced quickly if argon be introduced into the previously rarefied container. By successive evacuating and replacing the air by argon, the partial pressure of oxygen may be reduced to very small values.

The rate of dissociation of oxides differs in a stagnant and moving inert gas atmosphere, the mean partial pressure of oxygen being the same.

During dissociation of oxides in a stagnant inert atmosphere, close to the surface of the parts where decomposition of oxides is going on, the partial pressure of oxygen increases and may finally stop the process of dissociation despite the otherwise favorable mean partial pressure. Therefore, in the course of soldering, the main content of oxygen in a stagnant atmosphere will increase too. Removal of accumulations of oxygen near the places of intense dissociation of oxides favors maintenance of a certain minimum partial pressure in the container, and consequently, the continuous and spontaneous decay of oxides.

Some of the above-stated methods of reduction of the partial pressure of oxygen are now increasingly used in soldering, e.g. of titanium and its alloys with silver solders; this implies special containers filled with pure argon, previously dried, e.g. by passing it through titanium sponge at a temperature of 900°C. Heating in a pure inert gas atmosphere is used for tinning of titanium parts with reactive fluxes, containing AgCl , CuCl_2 , or SnCl_2 .

Soldering in a jet of pure argon may be used in the manufacture of stainless steel honeycomb structures.

Such structures are usually made of three or more layers filled with special filler and covered with a thin lining. The honeycombs may be square, hexagonal-shaped, etc. The filler made of stainless steel sheets 0.1-0.3 mm thick, and soldered to the lining, imparts rigidity to the structure without increasing its weight.

Honeycomb fillers are made of corrugated sheets, welded in a capacitor

type welding unit, or by means of welding tongs. Prior to soldering the foil-shaped solder is inserted between the filler and its lining.

IKh18N9T steel honeycomb panels may be soldered in a jet of pure argon without any preliminary nickel or copper plating of the surface to be soldered, using for this purpose lithium-bearing soldering alloys. Blowing of argon through the soldering containers is not interrupted even when cooling reaches a temperature of 100-200°C, as it prevents oxidation of the soldered seam.

For soldering of small-sized parts in an argon atmosphere (just as in soldering in a hydrogen medium), containers are fitted with a sand seal. To prevent piercing of the seal by the argon jet the separating faces of the container, after filling the seal with sand, are smeared with a compound of 1 part fine ground spongy refractory clay mixed with 2 parts of rubbed fire-clay, diluted to form a consistent water solution. Prior to soldering this layer is to be dried in air for 2-2.5 hours or in a drying oven at a temperature of 80-100°C. Drying in the oven should be associated with feeding of argon under a low pressure (2-3 units of the rotameter). In soldering large-size parts in an atmosphere of running argon, sealing of the container with sand seals is not reliable and must be replaced by sealing through welding.

Argon is fed into the container through a special connecting pipe which is welded to the container and which directs the stream to the back wall of the container. Discharge of argon occurs through another pipe flush-welded to the same wall as the feeding pipe connection (see Figure 120). Thus, after its admission in the container, argon mixes with residual gases left after air evacuation. Shape, position, and number of openings of the admission pipe are chosen to fit the work to be soldered so as to ensure complete mixing of argon with the gases inside the container, and an optimal surrounding of the work by argon. In passing through the container, the gas stream reduces the temperature inside the container. Therefore, temperature measurements in the furnace only, are insufficient, and should be supplemented by measurements in the container.

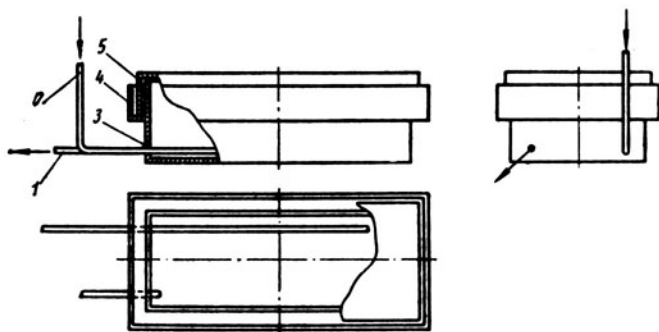


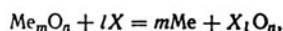
Figure 120. Container for soldering in an argon atmosphere:

- 1—discharge pipe for argon; 2—admission pipe for argon;
- 3—container; 4—sand seal; 5—cover.

For accurate readings, the thermocouple should be brought into the inner space of the container through the argon admission pipe, or through a special tube with a welded bottom. In containers continuously filled with a gas stream, the parts to be soldered are clamped by means of special fixtures, by pneumatic cushions, etc. For soldering of common copper, pure and dried nitrogen may be used as an inert gas atmosphere [23]. Cuprous oxides decompose in air only at a temperature of 2000°C. If heated in a jet of dry nitrogen, copper oxides are reduced at a temperature of 740-750°C; in such cases, soldering may be accomplished at this temperature, without any traces of copper brittleness.

§ 4. Soldering in a Reducing Gaseous Atmosphere

Soldering in a reducing gaseous atmosphere is based upon the fact that reaction between the solid oxides existing on the surface of the parts to be soldered and the surrounding gases, leads to reduction of the metal from its oxides and to removal of the new product of oxidation. This reaction may be written as



where X is a reducing agent.

Unlike vacuum soldering or soldering in an inert gas atmosphere, decomposition of oxides during soldering in a reducing atmosphere is not a spontaneous process but occurs by removing the oxygen from the oxides and combining it with other more easily removable compounds.

There are several methods of soldering in a reducing gas atmosphere. Most investigated is the soldering process in hydrogen. Soldering in other reducing gases (e.g. in Co, CH₄, etc) so far has fewer applications.

Soldering in a hydrogen atmosphere is based on the property of this gas to reduce oxides of certain metals according to the following chemical reaction



As a rule, during soldering, oxides and metals are in a condensed state; therefore, the constant of reaction may be written as

$$K_p = \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^n.$$

where $p_{\text{H}_2\text{O}}$ and p_{H_2} = partial pressures of water vapor and hydrogen respectively.

The equilibrium constant of this reaction is linked with the variation in free energy through the equation

$$\Delta F = -RT \ln K = -4.576 nT \log \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right). \quad (\text{b})$$

Variation of free energy of the reaction with the temperature is written as /1/:

$$\Delta F = A + BT,$$

where A and B are constants.

Equation (b) permits us to determine easily the equilibrium partial pressure of water vapor with respect to the pressure of hydrogen

$$\log \frac{p_{H_2O}}{p_{H_2}} = \left(-\frac{A}{4.576n} \right) \frac{1}{T} + \left(\frac{B}{4.576n} \right). \quad (c)$$

From there it results that, when the $\left(\frac{p_{H_2O}}{p_{H_2}} \right)$ ratio of a reversible reaction is greater than that in the surrounding gaseous atmosphere, reduction of oxides will take place, and conversely, when the $\left(\frac{p_{H_2O}}{p_{H_2}} \right)$ ratio of the reversible reaction proves to be smaller, oxidation of the metal involved will take place.

Consequently, the soldering process and decomposition of the oxides, are favored if partial pressure of the water vapor mixed with hydrogen is reduced below a definite value.

Partial pressures of water vapor and hydrogen may be expressed more conveniently by the dew point of the gaseous atmosphere found by experiment. Resorting to equation (c), one can find the relationship between the dew point and the temperature of the reversible reaction (a).

The relationship between the dew point of hydrogen and the temperature of the reversible reaction (a), varies with the given data for the calculation /24/, /25/.

The region of values of dew point and temperature, at right from the curves of the reversible reactions (a), corresponds to the condition of decomposition of oxides, and to the reduction of metal; the region at left corresponds to the condition of a progressive oxidation.

As shown by Figure 121, soldering of titanium, aluminum, and their alloys is connected with enormous practical difficulties, owing to the extremely low dew point required.

The data stated above are true only for soldering of pure metals. Oxides of metallic alloys are of more complex composition, and conditions of the reversible reaction between them and the reducing agents will differ from that of pure-metal oxides.

Some rough data on the reducibility of metallic oxides in the presence of hydrogen, may be obtained by comparing the heat of formation of oxides and of the water vapor: oxides having a smaller heat of formation than water vapor (115.6 kcal/1 mole O_2) are easily reducible, whereas other oxides do not lend themselves so readily to reduction, or are reducible at all.

When soldering in a hydrogen atmosphere, interaction between hydrogen and the metal or alloy involved should be taken into account, i. e. dissolution of hydrogen in metal at the soldering temperature, and a possible formation of usually brittle hydrides, or of water vapor which may lead to porosity in metals (e. g. hydrogen embrittlement in oxidized copper).

Lead, cadmium, tin, titanium, tantalum, zirconium, or niobium form hydrides in the presence of hydrogen /26/, and therefore, soldering of such metals in a hydrogen atmosphere should be avoided.

Many oxides form phases of variable composition, particularly in the presence of isomorphous oxides (e.g. Fe_2O_3 , $\alpha\text{-Al}_2\text{O}_3$ and also FeTiO_3 and NiTiO_3)

For the time being, no data on the variation of free energy of complex oxides (e.g. $(\text{Fe}, \text{Cr}, \text{Al})_2\text{O}_3$, or $(\text{Fe}, \text{Ni})\text{TiO}_3$) could be assembled. Certain alloys form oxides with their own components (e.g. Al-Mg alloys form (depending upon the magnesium content) the oxides Al_2O_3 and $\text{MgO} \cdot \text{Al}_2\text{O}_3$, or $\text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{MgO}$, or $\text{Al}_2\text{O}_3 + \text{MgO}$).

Data on the stability of pure metal oxides (provided the oxidation products of multicomponent alloys are composed of simple oxides) make it possible to judge the possibility of soldering such alloys in reducing gases. So, for instance, alloys which form MgO , TiO_2 , Al_2O_3 , $\gamma\text{-Al}_2\text{O}_3$, or BeO hardly may be soldered in a customary reducing atmosphere (hydrogen). Alloys which form oxides containing Cr_2O_3 or oxides of these metals ($\text{Cr}, \text{Fe})_2\text{O}_3$ require very dry reducing gases.

These assumptions are confirmed by practical experience. So, for instance, stainless steels of the 1Kh18N9T grade, forming upon oxidation mixed oxides $(\text{Cr}, \text{Fe})_2\text{O}_3$, or $\text{FeO}(\text{Cr}, \text{Fe})_2\text{O}_3$, may be soldered in an atmosphere of hydrogen or dissociated ammonium, only if all traces of oxygen, or carbon dioxide, are previously removed from the gaseous atmosphere, and the dew point of the latter does not exceed -60°C /24/, /27/ - /30/. Oxides of steel with a maximum content of 2% of Cr, Si, and Mg, cannot be reduced in a hydrogen atmosphere at temperatures below 1200°C . Steel with $\geq 2\%$ Ti also cannot be soldered in a hydrogen atmosphere. Soldering of carbon steels, may be done in a reducing atmosphere containing maximum 0.01% H_2O , or 0.01% O_2 , i.e. having a dew point of less than 50°C .

Apart from carbon steel such steel alloys as, high-speed, high-carbon, stainless or chromium-molybdenum steels, and the chromansil alloy may also be soldered in an atmosphere of hydrogen or dissociated (cracked) ammonium. Since oxide films on nickel-tungsten steels are subjected in a hydrogen atmosphere to intense reduction over a temperature range from 1180 to 1200°C , nickel-tungsten steels should not be soldered at such temperatures.

Hard alloys (of the VK2, VK3, VK6, VK8, VK10 and VK15 grade) composed of cobalt and tungsten carbides and containing 10 times more carbon as compared with steel alloys, may be soldered only in an extremely dry reducing atmosphere having an appreciable amount of hydrogen. The dew point of this atmosphere should not exceed 50°C /31/.

Certain instances of soldering in furnaces with a reducing atmosphere require the use of fluxing substances. This applies for the case where the gaseous atmosphere has an insufficient low dew point or is insufficiently active with respect to the oxides formed on the metal to be soldered.

So, for instance, hard alloys containing titanium carbides besides tungsten and cobalt carbide (of the T5K10, T14K8, T15K6, T30K4, or T60K6 grades) are soldered by the combined method of oxide removal and flux-soldering in a reducing atmosphere. The same method may be applied for the soldering of steel grades with an elevated content of Cr, Si, or V, e.g., the tool steels of the 40Kh, 9KhS, or R9 type. In such cases potassium fluoride dissolving the oxides of these elements may be used as a fluxing agent.

Soldering in a reducing atmosphere implies the use of fluxing agents not only when metallic oxides are formed which are not reducible by the given atmosphere, but also when the parts to be soldered or the solder contain volatile elements like Cd, or Zn.

In practice, pure hydrogen is seldom used for soldering purposes. Usually, the reducing atmosphere contains nitrogen, and sometimes CO_2 , NH_4 , H_2O , etc. Therefore, in deciding on the utility of such gases for reducing purposes, the possible interaction between them and the solder or the parts to be soldered, and their effect on the quality of the final joint should be taken into account.

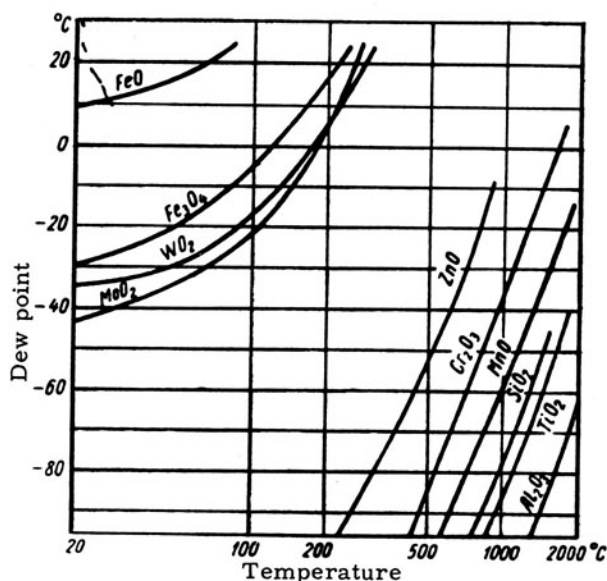
Except the inert gases argon and helium, such gases as H_2 , N_2 , CO , CO_2 or NH_3 , and their mixtures are able to interact with many metals, particularly at high temperatures.

The degree of interaction between the basic components of a reducing atmosphere, hydrogen and nitrogen, and the metals to be soldered depends on the composition of the base metal, the soldering temperature, and the atmospheric pressure.

Hydrogen is liable to be absorbed by all metals. In metals like Fe, Mn, Co, Al, Pt, Mo, etc, hydrogen is dissolved in the atomic state, forming solid solutions.

Figure 121.

Variation of the dew point of H_2 with the temperature of the reversible reaction (a) (according to Chang)



When absorbing hydrogen, certain alloys may undergo large changes in their properties. After absorbing hydrogen at a high temperature, steel parts upon cooling down to the room temperature, if subjected to impact bending tests, exhibit brittle fracture. This defect develops along the grain boundaries, although, after absorption of hydrogen, no visible structural changes of the steel parts could be noticed. Thus, reduction of brittleness of steel after absorption of hydrogen occurs only after reheating above the Ac_3 critical point [32]. After soaking structural steel for one hour in a hydrogen atmosphere with a dew point of $+30^\circ\text{C}$ at a temperature of 1200°C , it exhibits a considerable increase in brittleness due to absorption of hy-

drogen /33/. On the other hand, heating the same steel grade for one hour in a hydrogen atmosphere at a temperature of only 1000°C, or for 10 hours at a temperature of 750°C does not lead to any increase in brittleness. Neither could brittleness be noticed when structural steel was heated in a hydrogen atmosphere with a dew point of -35 to -45°C, at a temperature of about 1200°C and at a holding time of 10 hours. Data /34/ on the solubility of hydrogen in various steel alloys and metals refer to relatively stable conditions, and therefore are not always applicable to such a non-equilibrium process as soldering. However, the character of these processes most frequently develop in the same direction as in stable processes. Therefore, for judging the effect of the composition of the base metal and solder on their capacity to absorb hydrogen, the data obtained for stable processes also may prove to be useful. The ability of a metal to absorb hydrogen increases with the increase in temperature, and exhibits sudden alteration at isomorphous transformations, or changes of state. Figures 122-124 present data on the ability of certain steels and metals to absorb hydrogen at elevated temperatures and at a pressure of 750 mm of mercury /35/-/37/.

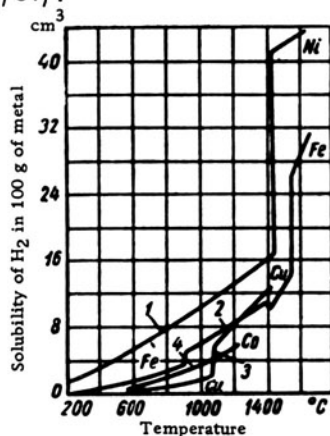


Figure 122. Isobars of solubility of hydrogen, in copper, nickel, cobalt, and iron for various temperatures

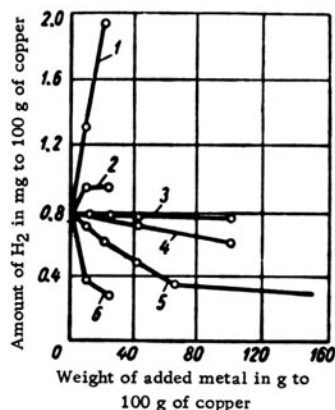


Figure 123. Variation of isobars of solubility of hydrogen in molten copper in dependence on the amount of inclusions:

1-nickel; 2-lead; 3-silver; 4-gold; 5-tin; 6-aluminum.

Certain metals (Cu, Ni, Co, Au, Ag), chemically inert towards nitrogen, do not dissolve the latter. Nitrogen combines with iron to form two nitrides, Fe_4N and Fe_2N . At a temperature of 550°C, Fe_2N dissociates in a medium of pure nitrogen. At a higher temperature Fe_4N dissociates also. Figure 125 shows the solubility of nitrogen in steel (iron) at a pressure of 760 mm of mercury.

Dissolution of nitrogen in metals begins at the temperature of its chemical interaction with the respective metals, i. e., at the temperature of formation of nitrides. Adsorption of nitrogen on iron is not accompanied by a complete dissociation of the gas molecules, but its dissociation in a gaseous atmosphere constitutes a preliminary stage of adsorption; the concentration of nitrogen in steel is thereby proportional to the concentration of atomic nitrogen in the gaseous phase. Therefore, adsorption of

N_2 does not occur at low temperatures when thermal dissociation of nitrogen molecules is insignificant.

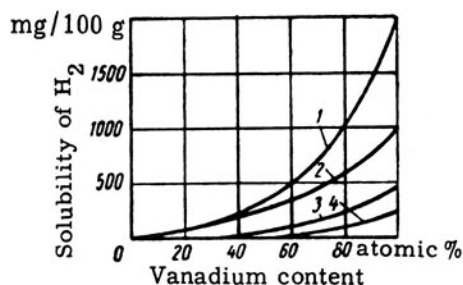


Figure 124. Isobars of variation of solubility of hydrogen in vanadium steel with the temperature and composition of the alloy:

1—at 500°C; 2—at 600°C; 3—at 800°C; 4—at 1000°C

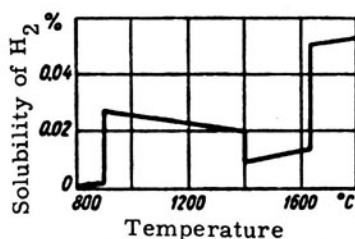
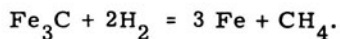


Figure 125. Isobars of variation of solubility of nitrogen in steel at a pressure of 760 mm of mercury

Ammonium, decomposing on the surface of steel parts retains on them the elevated concentration of atomic nitrogen and favors dissolution of nitrogen in steel.

When soldering steel parts in furnaces with a nitrogen-hydrogen atmosphere, a nitride coating forms on their surface. If soldering occurs at high temperatures and with a relatively reduced holding time, the thickness of the nitride layer is rather reduced. So, for instance, the thickness of the nitride layer on 9KhS steel heated for 15 min up to 900°C in a gaseous atmosphere containing 6% ammonia, does not exceed 0.1 mm; at a temperature up to 1000°C, 0.15 mm and at temperatures up to 1100°C, the thickness is 0.35 mm [31]. When steel is soldered in a reducing atmosphere containing hydrogen, it reacts with the carbon of the steel part according to:



This reaction yields volatile methane and causes decarburization of the steel.

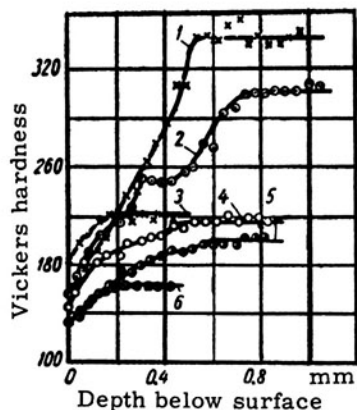


Figure 126. Effect of the reducing atmosphere on the degree of decarburization of steels with a different carbon content. Holding time 3 hours at 850°C:

1—1.2 % C; 2—0.8 % C; 3—0.15 % C and 1 % Cr;
4—0.04 % C and 1 % Cr; 5—0.4 % C; 6—0.15 % C,

It was found [38] that an increase in the temperature and in the holding time at that temperature, favors the decarburization process. In this, humidity of the reducing atmosphere plays an extremely important part. In order to prevent strong decarburization of steel in the course of soldering, a dry reducing gas with a maximum content of 0.1 % H_2O (by weight) should be used. Figure 126 contains some data on the decarburizing effect of dried hydrogen on steel parts as a function of temperature and carbon content.

The process of decarburization in an atmosphere of dissociated ammonium, may to a great extent, be slowed down by adding to this atmosphere no more than 1 % methane or 3 % propane; on the other hand, this may lead to a certain evolution of soot.

The decarburizing effect of the reducing atmosphere becomes particularly noticeable in the soldering of high-carbon steels; this sometimes implies the recarburizing of hardenable steels after soldering.

Complete elimination of the decarburizing effect in furnaces with reducing atmosphere cannot be achieved.

The activity of reducing gaseous atmospheres largely depends on the concentration of hydrogen, carbon monoxide and moisture in those atmospheres. So, for instance, a visible reduction of ferrous oxides in a gaseous atmosphere at high temperatures, occurs only if this atmosphere contains at least 4 % H_2 or 12 % CO . Presence of moisture in the gaseous atmosphere is liable to diminish the reducing effect of the atmosphere, and to favor absorption of hydrogen by steel [24], [27].

§ 5. Composition and Preparation of Hydrogen-Bearing Reducing Atmospheres

The method of soldering in reducing gaseous atmospheres appeared as a result of investigations made by N. N. Beketov who was the first to reveal the possibility of reduction of metallic oxide films in a hydrogen atmosphere. The first practical application of these ideas was achieved as early as 1912 /42/ in the soldering of molybdenum discs to steel rods used in automation. At present this method has gained widespread acceptance, particularly in soldering copper to steel.

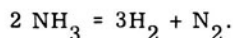
Replacing of manual and electric-arc welding by soldering in a reducing atmosphere, increased the efficiency 5-7 times when using batch-type heating furnaces, and 10-12 times, when using conveyor-type heating furnaces /43/.

Though less efficient than soldering in special furnaces, soldering of alloy steels and certain alloys in containers filled with dry hydrogen or dissociated ammonium is used largely in joining stainless steel or other alloys.

At present, soldering in a reducing hydrogen atmosphere is widely used in the aircraft and automobile industry, for construction of electrical equipment, etc. This method has found wide applications in soldering turbine blades, bicycle frames, medical instruments, platinum or tungsten contacts, copper conductors, electrical lamps, radio-tubes (valves) hard alloy tips and tools, soldering of ceramic to steel linings of brake systems, etc. In the U. S. A., soldering in furnaces with reducing atmosphere is employed in the manufacture of pipe lines, parts of steam ships, airscrew (propeller) blades and sleeves, parts of automobile carriages, and turbine discs, etc.

Hydrogen is the most active gaseous reducing medium; nevertheless its use is costly and not free of danger. Hydrogen is stored in special bottles under a pressure of 150 atm. When mixed with oxygen in a concentration ranging from 4.1 to 74 %, hydrogen is highly explosive, and therefore soldering in a hydrogen atmosphere has only a few applications; most frequently hydrogen is replaced by gaseous products, obtained from the dissociation of ammonium, which are the most suitable substitutes of hydrogen for soldering purposes.

Liquefied ammonium is stored under a pressure of 15-16 atm, in yellow bottles. A single bottle of ammonium, holding 40 l, replaces 12 bottles of hydrogen. Dissociation of ammonium is carried out at a temperature of 600-650°C in special dissociation units (Figure 127) by means of a catalyst composed of minute steel cuttings and natural or synthetic magnetite. The reaction of dissociation has the following form



The resulting mixture of 75 % hydrogen and 25 % nitrogen (by volume) is less explosive than pure hydrogen.

Other reducing media besides hydrogen and products of dissociation of ammonium are the products of incomplete combustion of air-gas mixtures, e.g. town or producer gas, natural gas, bottled propane, water gas, products of pyrolysis of kerosene, products of incomplete combustion of gases obtained from peat gas-producers, etc. Such mixtures contains /39/:

25 % CO; 2-3 % CH₄; 9-10 % CO₂; 0.2 % O₂; 18-20 % H₂ and the remainder, N₂. A reducing mixture obtained by burning (at an air volume/gas volume ratio = 2.5) town gas after its drying and cleaning, has the following composition: 5 % CO₂; 10 % CO; 15 % H₂; 0.3 % CH₄ and the remainder, N₂.

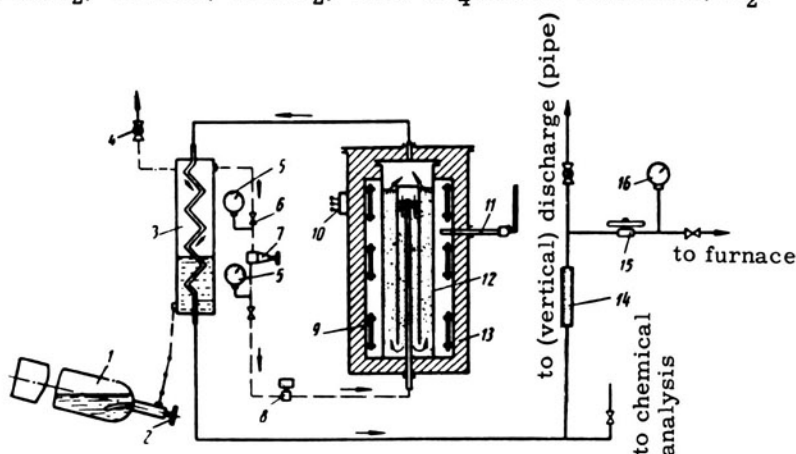


Figure 127. Flow diagram of the plant for preparation of dissociated ammonium (DA) from anhydrous ammonium:

1—ammonium bottle; 2—discharge valve; 3—pressure vaporizer; 4—discharge safety valve; 5—pressure gage; 6—disconnecting valve; 7—high pressure reduction valve; 8—solenoid valve; 9—electric heating elements; 10—terminals of electric heating elements; 11—thermocouple; 12—converter filled with catalyst; 13—dissociating apparatus; 14—gas flow-meter; 15—low-pressure regulator.

Similar gas mixtures are suitable for soldering only low carbon steels with copper solders. Their relatively low hydrogen and carbon monoxide content makes them unsuitable for soldering alloys which form chromium oxides upon oxidation. For reduction, these alloys require hydrogen or dissociated ammonium. There are several special industrial plants for preparation of gaseous reducing atmospheres.

The PAO-40 and PAO-80 type plants have an output of 40 and 80 m³/hr respectively.

The AA-60 industrial plant for dissociation of ammonium has a production rate of 60 m³/hr and furnishes a gas mixture necessitating additional drying to drive off traces of moisture. Moisture removal from hydrogen, dissociated ammonium, or from the combustion products of high-grade gaseous fuels is usually carried out in special drying units. In these dryers, the gaseous mixture is conveyed through a layer of granulated silicagel or alumogel both active absorbers of moisture and able to be re-claimed if heated up to 150-250°C. By drying gaseous mixtures in these substances, the dew point drops to -50°C. In order to obtain a still lower dew point, the gaseous mixture is additionally conveyed through special vessels filled with anhydrous phosphorus which is the strongest drying agent known, capable of insuring a sufficiently low dew point (-80°C). In order to improve conveying of the gaseous mixture through the vessel, anhydrous phosphorus is mixed with porcelain breakage (size of pieces 10-15 mm).

Other methods for removal of moisture from reducing atmospheres may also be mentioned: after drying with granulated silicagel, the gaseous mixture is subjected to a sudden cooling to condense residual moisture; in another method, hydrogen is passed through a couple of special drums, one of which contains granulated alkalis, caustic soda or potassium. In the other drum, filled with copper sponge heated up to 350°C, the gaseous mixture is cleaned again. The gas mixture is then conveyed through a special vessel (the so-called drying vessel). After this final stage of drying, hydrogen contains only one thousandth or one ten thousandth of a per cent of moisture and oxygen.

The partial pressure of oxygen in the gaseous inert or reducing atmosphere may be achieved*, not only by using chemically active oxygen absorbers, but also by applying catalysts capable of combining the oxygen with hydrogen and with the water vapor driven off from the gaseous mixture during drying of the latter. Platinum and palladium have the best catalytic properties. As was found by M. B. Ravich, the dunite mineral containing traces of native platinum, osmium, iridium, and also ferrous oxides, constitutes in the atomized state, a catalyst in the combustion process of gases. R. Esinberlin used this mineral as a catalyst in removal of oxygen ingredients from a hydrogen-nitrogen mixture, in order to obtain a reducing atmosphere for soldering of metals.

Drying of hydrogen only or cleaning hydrogen of oxygen ingredients only, proves to be insufficient for reduction of the soldering temperature. After a step-by-step removal of oxygen ingredients from hydrogen, by passing the mixture through a container filled with fine-ground dunite heated to 550°C, followed by drying the gas to a dew point of -80°C in a mixture of silicagel and anhydrous phosphorus, a suitable gaseous reducing atmosphere can be obtained for soldering structural 30KhGSA steels at 800°C with the PSr72 solder, and for soldering at 750°C with the PSr48KN solder; this solder spreads on copper, nickel or pure iron at a temperature of 650°C.

Figure 128 illustrates schematically an experimental plant devised by R. L. Esinberlin for the soldering of steel parts in a nitrogen-hydrogen atmosphere.

In such a mixture (< 10 % H₂ and the remainder, N₂), previously cleaned of oxygen admixtures in a dunite catalyst, and of water vapor in a mixture of silicagel-phosphorous anhydride, 1Kh18N9T stainless steel, and heat-resisting EI435 alloys may be soldered over a temperature range from 1050 to 1080°C.

Soldering of low alloyed steels at a temperature of 650-660°C, requires preliminary nickel-plating (layer thickness ~ 1 micron) of the parts) In the previously described mixture of nitrogen-hydrogen, soldering of steel with brass solders may be achieved at a temperature of 920-950°C.

Sometimes, removal of traces of oxygen or moisture from hydrogen may be achieved by means of platinum-coated asbestos, or activated aluminum oxides, which assure a dew point of the gaseous mixture down to -60°C. Palladium catalyst treatment with subsequent conveying of the mixture through a bed of activated aluminum oxides for absorption of the remainder of the moisture may be used for the same purpose. The latter method makes it possible to obtain a dew point as low as -80 to -100°C [28].

* [It is obviously a missprint and should read "diminished"].

The dew point of the reducing atmosphere may be determined by means of the IIG-1 apparatus. For this to be done, a gas jet, in passing through the casing of the apparatus, touches a mirror connected to a copper bar, the other end of which is immersed in liquid nitrogen or in frozen acetone; the temperature of the mirror surface is then measured by a special thermocouple. That temperature on the mirror surface, at which appearance of a misty deposit can be noticed, is the dew point of the gaseous mixture involved.

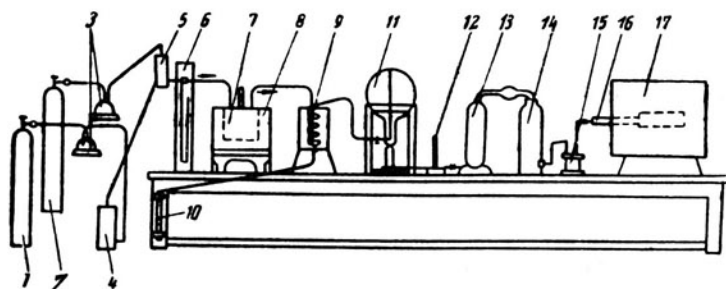


Figure 128. Diagrammatic representation of the experimental unit for removal of moisture and traces of oxygen from a nitrogen-hydrogen mixture:

1—hydrogen bottle; 2—nitrogen bottle; 3—gas counter; 4—flame-quenching device (flame trap); 5—gas mixer; 6—pressure gage; 7—catalyst; 8—electric furnace; 9—pipe coil; 10—header; 11—apparatus for measurement of residual O_2 ; 12—thermometric device for measuring the temperature of gas leaving the apparatus under 11; 13—vessel filled with silicagel; 14—vessel filled with phosphor anhydride; 15—humidimeter for measuring moisture of the gaseous mixture; 16—container; 17—furnace for electric soldering.

Cleaning gaseous mixtures of CO_2 and H_2 obtained in burning high-grade gaseous or solid fuel, is carried out in a solution of monoethanolamine. The factory types of the PAO-40 and PAO-80 plants for preparation of gaseous reducing atmospheres include special equipment for removal of CO_2 and traces of moisture from the gas mixture. The dew point of gaseous mixtures produced at these plants reaches $-40^\circ C$.

§ 6. Technology and Equipment for Soldering in Gaseous Reducing Atmospheres

The unit for soldering low-alloyed steels with copper solders in a reducing atmosphere, usually consists of three parts; electric furnace, control and adjustment equipment, and a gas source. A common feature of these furnaces is the cooling chamber for preventing formation of scale during cooling of the parts. The cooling chamber possesses double walls through which cooling water runs. In order to reduce air infiltrations the

chamber doors are placed below the level of the hearth bottom of the heating chamber. Distortions of the work at sudden temperature changes may be avoided by gradually raising the temperature to the melting point of the solder. In the first two zones of the heating chamber of the furnace, the pre-heating and the heating (the central) zone, the temperature is below the melting point of the solder, but the oxides formed on the surface of the work are here completely reduced. In the third zone of the furnace the solder is molten and fills the gap. In the cooling chamber the parts are cooled in a protective atmosphere or are fed into the hardening tank (Figure 129).

The bottom hearth of the furnace is essentially a graphite or steel plate. A ceramic hearth is less suitable, due to lower resistance to heat deformations caused by sudden changes in temperature.

Heating of the work prior to soldering is done either in batch furnaces or in continuous (conveyor-type) furnaces. Usually, batch furnaces are used for soldering large and heavy parts, for soldering odd shaped parts, or for laboratory applications. The heating chamber of such furnaces is separated from the cooling chamber by a refractory shielding door; the doors, placed at the ends of the furnace are tightly closed after charging the work into the furnace.

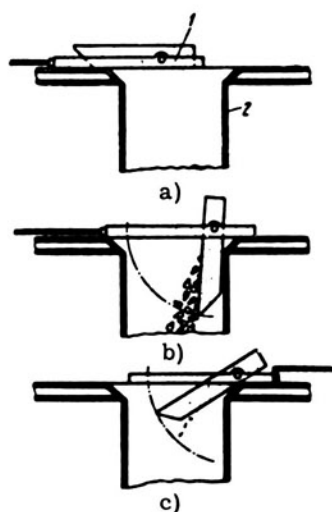


Figure 129. Working diagram of the setup for hardening after soldering in furnaces with a reducing atmosphere:

- a) position prior to feeding of the parts into the hardening tank;
- b) while feeding the parts into the tank; c) after feeding the parts into the tank; 1—appliance; 2—hardening tank.

Soldering of medium and small-sized parts in serial production is more conveniently done in furnaces equipped with wire belt-conveyers (Figure 130), while soldering of large and heavy regular shaped parts is

better done in roller-hearth furnaces. The conveyor type furnaces do not differ in design from the batch type furnaces. The conveyor belt is made of heat-resistant steel, or (iron free) nichrome and mounted on the bottom of the heating chamber. The roller hearth is composed of rollers linked to form an endless chain mounted along the walls of the heating and cooling chambers. The roller table is enclosed in a gas-tight housing. The parts to be soldered are fed to the roller table (Figure 131). During continuous movement of the roller table, the charging doors of the furnace are open. In order to prevent air infiltration in the gaseous atmosphere inside the furnace before the heating chamber and at the end of the cooling chamber, special sluice-type chambers are mounted. The front and rear ends of the cooling chamber are covered by special asbestos or glass silk curtains.

Heating of the electric batch type or conveyor type furnaces is achieved by means of metallic or ceramic heating elements. Nichrome heating elements permit heating up to a temperature of 1100°C . Ceramic (selite) heating elements assure a heating temperature up to 1300°C . Both types are used in Russian industry.

Heating of steel parts, 400×350 mm, for soldering with copper solders is accomplished in the KVP-60 type conveyor furnace assuring a maximum heating temperature of 1150°C . Figure 132 shows distribution of heat in the heating chamber of this furnace. Heating of parts with maximum cross-section of 200×350 mm, is done in the OKB-147 walking beam type furnace which insures a maximum heating temperature of 1150°C . The production rate is up to 60 kg/hr.

The furnaces are equipped with ceramic or metallic muffles. A peculiar feature of metallic muffles is their rapid heating: they are brought up to the soldering temperature in 1.5-2 hours; on the other hand, their service life is limited. Metallic muffles are made of chromansil, chromemoly steels, stainless steel, or armco-iron.

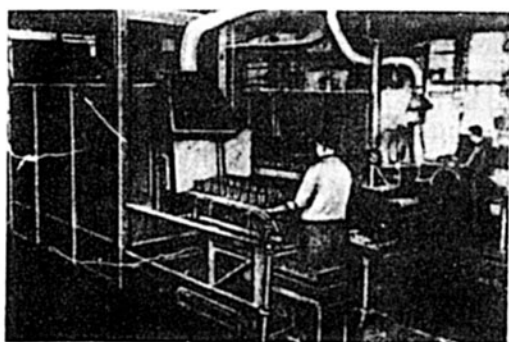


Figure 130. Conveyor type furnace for soldering in a reducing atmosphere

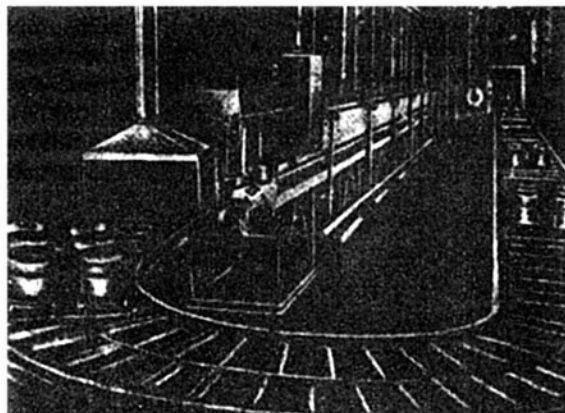


Figure 131. Roller-hearth conveyor furnace

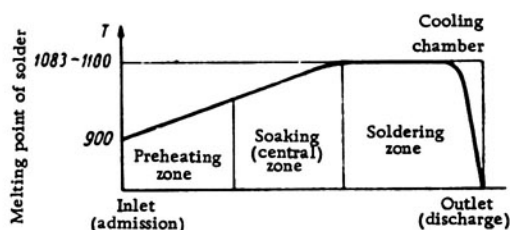


Figure 132. Distribution of heat in the heating chamber of the KVP-60 conveyor-type furnace with reducing atmosphere

Ceramic muffles have a much longer service life, but their heating time is three times longer than that of the metallic muffles. Ceramic muffles are heated by means of a nichrome or molybdenum heating element wound on the muffle and coated with a special compound (layer thickness, 5-8 mm), dried at a temperature of 150-200°C. The compound may be prepared of different grades of corax* mixed with 5-8 % Latin clay or with Chasow-Yar clay. This compound prevents oxidation of the molybdenum heating element in a hydrogen atmosphere.

The pressure of the gas atmosphere is measured by means of water gauges; also, the furnace is provided with gas flow-meters. When using dissociated ammonium, a special apparatus (dissociometer) for measuring the degree of dissociation should be provided.

Furnaces in which low alloyed steel is soldered with copper solder are unsuitable for soldering high-alloyed steels since the latter are covered with oxides reducible only in a very dry atmosphere of hydrogen or

* [Translator's note: a kind of white electro-corundum].

dissociated ammonium. The customary ceramic furnace lining, and the loosely closed charging doors of the furnace do not allow the use of a controlled atmosphere having a sufficiently low dew point. Therefore, parts made of alloys or special steels which can be soldered only in a hydrogen or dissociated ammonium atmosphere, sufficiently free of oxygen or water vapor, usually are soldered in hermetically closed containers placed in horizontal or vertical batch furnaces, or sometimes in vertical soaking pits. Containers are made of medium carbon, stainless or heat resistant steel sheets, with a wall thickness of 1.5-2 mm. The container consists of a box filled with the parts to be soldered, a cover, and pipes welded to the cover or the box, for admission and discharge of the gas, and for the thermocouple. Sealing of the container is achieved by welding the cover to the box, or by filling the gap between the cover and the box with dry calcinated sand.

Efficiency of soldering in hermetic containers is lower as compared with direct charging in a furnace with a reducing atmosphere, but this method offers possibilities for the reduction of stable oxides formed on the surface of high-alloyed steels and certain other alloys.

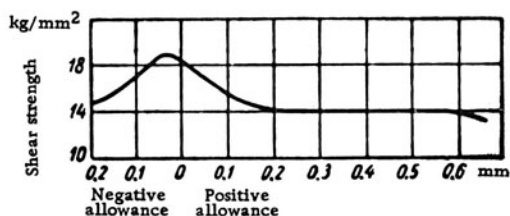


Figure 133. Variation of shear strength of copper-soldered test specimens, with the gap width /40/

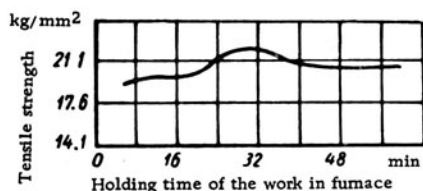


Figure 134. Relation between tensile strength of copper lap-soldered steel test specimens, and their holding time /43/

Quality of joints soldered in containers with a reducing atmosphere depends on the proper selected type of joint, the magnitude of the clearance between the parts, the preparation of the surface in view of soldering, the proper choice of the soldering alloy, and the soldering technique (composition of the gaseous medium, soldering temperature, and holding time in the furnace).

In choosing the proper solder, requirements the joint has to meet, should be borne in mind. As a rule, soldering of low-carbon and low-alloyed steels is done with copper solders having an excellent wetting power and penetrating into the extremely small gap resulting from an interference fit. High-strength soldered joints are obtained at a negative allowance of 0.038 mm (Figure 133). If instead of high mechanical strength, tightness of the joint is required, clearance between the parts may reach 0.5 mm. Figure 133 illustrates the shear strength of low carbon steel joints, soldered with different clearances.

In furnaces having a dissociated ammonium atmosphere, soldering is done with wire-shaped solders or with a soldering paste composed of two parts electrolytic copper-wire powder and one part glycerine. This paste should be applied on the seam area in a thin evenly distributed layer, sometimes by means of a special atomizer.

Duration of soldering is 25-30 min; after soldering, the conveyor is brought in to the cooling pit where the parts are cooled in a reducing atmosphere to 100-200°C.

Copper-soldered parts may be subjected to hardening. Soldering of steel parts may be made with silver solders having the same flowability as copper solders. Silver-alloy solders have a smaller spreadability than pure copper or silver; besides, due to the presence of cadmium and zinc, both low volatilizing elements, soldering in a controlled atmosphere implies the use of fluxes.

Soldering hard alloys to steel parts in a reducing atmosphere requires, besides copper solders, a series of other soldering alloys: aluminum-manganese bronze, manganese or nickel brass, and L62 brass solders. L62 brass and manganese bronze have the best spreadability /31/. Joints made of alloy steels, or of special nickel or iron alloys and designed to work at high temperature or in corrodant media, should be soldered with special solders which assure joints with the required properties.

Sometimes the area of spreading of the molten solder should be limited in view of welding after furnace-soldering; otherwise the solder entrapped in the welding zone is liable to cause leakages and cracks in the soldered seam. Therefore, after soldering of such parts, any excess solder should be removed by grinding, pickling, etching, etc*, operations which increase the manufacturing cost (prime cost) of the work. Solders like copper, PSr40, or other alloys, have a particular strong spreadability on steel base-metals.

If steel parts are soldered in furnaces with a reducing atmosphere, the spreading of the molten solder may be limited, since copper and some other solders have a poor spreadability on steel surfaces previously treated by polishing, chromium plating, or coated with chromic acid applied on a clean, polished surface. If on an oxidized steel surface, chromic acid is applied, the ferrous oxide under the effect of a reducing atmosphere, will be reduced to pure, iron sponge, through the pores of which beneath the layer of chromic acid, molten copper solder is liable to penetrate.

Spreadability of molten copper may also be adjusted by altering the hydrogen content of the gaseous furnace atmosphere; reduction of the hydrogen content lowers spreadability of molten copper on steel surfaces.

* [Translator's note: pickling and etching in the sense used by the Russian authors have the same meaning].

Spreading of copper may also be limited by placing the copper solder in special grooves provided in the gap, where the molten solder gathers.

Where soldering is carried out in furnaces or in containers filled with hydrogen-bearing gaseous mixtures special precautions should be taken to prevent explosions.

Explosion of an air-hydrogen mixture is likely to occur at a content of 4.1-74% H_2 . Deflagration takes place when the temperature, at least at a single point of the mixture, reaches a definite value in the range from 590-625°C, depending on the hydrogen content. In order to prevent explosion hazards during starting of the furnace, its chambers prior to soldering, should be completely filled with the gaseous mixture at 0.1-0.15 atm pressure above atmospheric pressure. During working of the furnace, at the discharge end of the furnace a control gas-flame should be permanently ignited to indicate presence of gas inside the furnace. The danger of propagation of the gas flame through the furnace chamber may be avoided, by imparting to the gas jet emerging from the furnace a velocity equal to or surpassing several times the velocity of flame propagation. After disconnecting the furnace, a gas jet is passed through the latter until the temperature of the gaseous mixture decreases below the deflagration point of this mixture; upon reaching this temperature, delivery of the gas is stopped. If, after soldering, a very clean surface of both the parts and the soldered seam is required, gas blowing through the furnace should be continued until the furnace is cooled down to 250-300°C. A reducing gas mixture is fed in the same manner through the container but the hydrogen mixture is ignited at the end of the discharge pipe.

In order to prevent explosions of the gas mixture in the furnace, sometimes an inert gas stream is blown through the furnace; for this purpose, carbon dioxide, nitrogen, or (oxygen free) products of smokeless combustion of industrial gases, may be used.

Admission of a hydrogen mixture in a furnace heated to a temperature above 750°C is practically free of any danger, but a gas mixture fed into a furnace heated below 750°C may lead to explosions.

After starting operation of the furnace, the parts, ready assembled for soldering, are charged into the furnace through a charging hole. After holding at the required temperature, the parts are transferred to the cooling chamber and removed from the latter upon reaching a temperature of 200°C.

In conveyor furnaces, the parts placed on the conveyor belt pass through the whole heating cycle as the conveyor moves with them through both furnace chambers.

When soldering is achieved by means of containers, the soldering process develops in the following manner: the parts assembled for soldering are placed in the container; the cover is then welded to the body at the seam line or filled with calcinated sand. Right after being charged into the furnace, the container is filled with hydrogen but previously the container should be purged with a nitrogen jet. The holding time of the filled container varies from 10 to 60 min depending on the sizes of the container and the parts to be soldered. After completion of soldering, the container is withdrawn from the furnace, continuously being purged with a reducing gas jet.

The choice of proper soldering temperature and holding time, is of paramount importance in obtaining a high-quality soldered joint. The sol-

dering temperature should not drop below a definite value. Holding time at the soldering temperature should not be too high in order to prevent intense dissolution of the base metal in the molten solder, but on the other hand, it should not drop below a certain value which is necessary to assure a rigid metallic bond between the solder and the base metal along the whole seam area. The optimal holding time for a given joint is not always the optimal time for given properties of the base metal. A holding time of 30 min may assure a strong soldered joint but, as is known, it may lead to a considerable growth of the crystalline grain, and thus to certain deterioration of the properties of the base metal (steel).

Table 83 /40/ presents a synoptic view of typical defects and their causes, which may be encountered during soldering in furnaces with a reducing atmosphere.

The holding time for parts 1 mm thick usually varies from 5 to 10 min; at a thickness of 2-3 mm, the holding time is 10-15 min. The holding time at the soldering temperature of parts with larger wall thickness varies between 20 and 30 min /21/.

The average tensile strength of steel parts soldered with copper solders at a soldering temperature of 1125°C and a holding time of 10 min is 66 kg/mm², and at a holding time of 30 min, 87 kg/mm².

Table 83

No.	Kind of defect	Causes of its appearance	Measures to prevent defects
1	Though the solder melts, it does not form a fillet (bead) on the opposite part of the seam	Capillary flow in the gap between the parts is disturbed	Use a less tight fit, try a larger clearance
		Insufficient holding time during soldering	Increase holding time in the furnace
		Untimely solidification of the molten solder due to dissolution of the base metal in the solder	Increase soldering temperature
		Surface of the seam inadequately cleaned	Clean the components thoroughly prior to assembling. Preflux the seam
2	The solder does not wet the base metal	Air infiltration in the heating space	Increase the rate of delivery of the gas in the furnace; increase the hydrogen content of the furnace atmosphere. Raise the charging door to a smaller height, and open less frequently. Preflux the surface of the work. Copper plate the parts (if copper solders are used).

Table 83 continued

No	Kind of defect	Cause of appearance	Measures to prevent defects
		Insufficient roughness of the surface	Roughen the surface by pickling, abrasive-cleaning with emery cloth, shot-blasting, grinding, mechanical cleaning
		Work placed in the furnace at an unfavorable angle	Place the work at the right angle
3	Solder does not flow into the gap though the seam is wetted	Rolled up flashes prevent solder from flowing into the gap	Correctly place the work so as to insure flowing-in of the molten solder. Place solder over the seam or against the shoulder. Apply solder paste on the seam or preplate the seam with a soldered coating
4	Gap is liable to enlarge during soldering in the furnace	Press-fit used too tight	Widening the gap prior to soldering
		Non-uniform heat-expansion of the work due to a dissimilar metal composition, or a varying cross-section	In designing the proper gap, occasional expansion during heating should be allowed for.
		Stress relieving due to cold-hardening	Change the method of fixing the work for soldering
		Lowering of the unsupported part, thus leading to its bending at elevated temperatures	idem
5	Insufficient tightness of the soldered seam though apparently good filling of the gap with molten solder	Opening of the seam during soldering	See measures §4
		Insufficient compactness of the solder	Check the compactness of the solder
		Varying width of the gap	Assure a close fitting of the members of the joint and a constant width of the gap

Table 83 continued

No	Kind of defect	Cause of appearance	Measures to prevent defects
6	Weak seam though good filling of the gap	Burning of the metal during welding of the work in view of its clamping	Clean the parts thoroughly prior to assembling. Provide ample quantity of flux around the gap and within it
		Gap is too large	Reducing the width of the gap
		Expansion of the gap during heating	See measures §4
		Impurities in the soldered seam	—
		Insufficient holding time in furnace	Increasing of holding time during soldering
		Intense heat-treatment after soldering (by heating in a cyaniding bath or quenching in water)	Avoid intense heat-treatment after soldering
		Relative displacement of the members of the joint during solidification of the solder	Take measures to avoid displacement of the parts during solidification of the solder
	After withdrawal of the work from the furnace it is slightly oxidized, though it should have a bright surface	Insufficient amount of hydrogen in the reducing atmosphere, or of carbon dioxide in the cooling chamber	Check operation of the cooler and regulator of the composition of the gaseous atmosphere. If necessary, clean the condenser tubes, reduce humidity of the atmosphere. Increase velocity of the gas delivery. Avoid currents of air in the room
		Intense overheating of the work in the furnace	Intensify the water delivery through the cooling chamber of the furnace. Slow down velocity of transfer of the work through the furnace. Reduce amount of heat evolved from the flame curtain at the discharge end of the furnace, if a protection curtain is available at the furnace end

Table 84

Soldering of metals and alloys in an inert gas atmosphere

Type of gaseous atmosphere	Dew-point °C	Composition of gaseous atmosphere, in %				Solder	Base metal
		H ₂	N ₂	CO	CO ₂		
Combustion products of fuel gas (low content of hydrogen)	7	5-1	87	5-1	3-11	Silver, brass, phosphorus-copper	Brass, copper
Combustion products of fuel gas (decarburizing medium)	-7	14-15	70-71	9-10	7-4	Copper, silver, brass, phosphorus copper	Copper, brass, low-carbon steel nickel, monel metal, medium-alloyed steel (rapid heating in order to avoid carburizing)
Combustion products of gaseous fuel (dried)	-40	15-16	73-75	10-4	2-5	idem	idem and high-carbon steels, nickel alloys
Combustion products of fuel gas (carburizing medium)	-40	38-40	41-45	17-15	4-0	idem	idem
Dissociated ammonia	-54	75	25	-	-	idem and nickel-chromium-base solders	idem and chromium alloys
Hydrogen (fed from bottles)	-7	97-100	-	-	-	Copper, brass, silver, phosphorus copper	Copper, brass, low-carbons and medium-carbon steels, monel metal
Dry and pure hydrogen	-60	100	-	-	-	Silver, phosphorus-copper, copper, brass, nichrome	idem and alloys and steels alloyed with chrome tungsten, or carbides of metals

In order to eliminate the effect of heating conditions of the soldering process on the properties of the soldered joint, sometimes the work is subjected to heat treatment subsequent to soldering, but only if the temperature of the heat treatment does not exceed the temperature at the beginning of melting of the solder. With a proper assembling and preparation of the work, the joint of low-carbon steel parts soldered with copper solders in a reducing atmosphere, attains a mechanical strength of 16-21 kg/mm² /27/.

Test specimens of 1Kh18N9T steel soldered with copper solders at a temperature of 1100-1150°C and a holding time of 10 min, when subjected to a short time fracture test, exhibit a tensile strength of 32-35 kg/mm² and are absolutely air-tight at a test pressure of 20 atm /41/.

Table 84 presents general data about soldering of metals and alloys in furnaces with a reducing gas atmosphere.

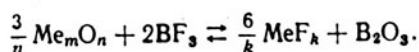
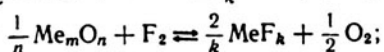
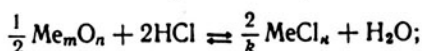
§ 7. Gaseous Reducing Atmospheres Without Hydrogen

At present, based on thermodynamic calculations, certain gaseous atmospheres may be considered for use as reducing media in the soldering process.

The thermodynamic criterion of reducibility of oxides exposed to the action of a definite gaseous atmosphere may be formulated in the following way: the strength of chemical bond of the reduction products must be greater than the strength of the bond in the oxide; in other words, if the change in free energy during formation of the products of reduction and of the oxide at a given temperature has a negative value, the gas atmosphere entering the reaction may become an oxide reducing agent. In this case, it is necessary that during soldering, the products of reduction be in the gaseous state.

As shown by the data presented in Figure 118 (according to /44/) on the variation of free energy of formation of oxides, carbon acting according to the reaction, $2C + O_2 = 2CO$, may become a strong reducing agent during soldering. For the time being, this fact has little practical application in the soldering technique.

As shown by thermodynamic calculations, chlorine, fluorine, hydrogen chloride, or trichloride of boron may be used as reducing agents in the soldering of a series of metals. The so-formed products of reaction at high temperature are mostly in the gaseous state. The reaction involved may be written as follows:



Tables 85-87 present certain results of thermodynamic calculations which show the possibility of using different gaseous atmospheres for reduction of oxides. The data have been computed assuming the pressure of the gaseous atmosphere to be equal to 1 atm /44/.

Table 85

Variation of free energy during the reaction of oxides with chlorine /44/

Type of reaction	Variation of free energy at different temperatures, in kcal	
	500°	1000°
$\text{Ag}_2\text{O} + \text{Cl}_2 = 2\text{AgCl} + \frac{1}{2}\text{O}_2$	-46.200	—
$\text{PbO} + \text{Cl}_2 = \text{PbCl}_2 + \frac{1}{2}\text{O}_2$	-24.100	-25.00
$\text{CdO} + \text{Cl}_2 = \text{CdCl}_2 + \frac{1}{2}\text{O}_2$	-21.20	-22.700
$\text{Cu}_2\text{O} + \text{Cl}_2 = \text{Cu}_2\text{Cl}_2 + \frac{1}{2}\text{O}_2$	-15.000	-12.500
$\text{MnO} + \text{Cl}_2 = \text{MnCl}_2 + \frac{1}{2}\text{O}_2$	-12.300	-9.900
$\text{NiO} + \text{Cl}_2 = \text{NiCl}_2 + \frac{1}{2}\text{O}_2$	-9.200	-6.400
$\text{ZnO} + \text{Cl}_2 = \text{ZnCl}_2 + \frac{1}{2}\text{O}_2$	-8.900	-17.600
$\text{SnO} + \text{Cl}_2 = \text{SnCl}_2 + \frac{1}{2}\text{O}_2$	-8.500	-16.600
$\text{FeO} + \text{Cl}_2 = \text{FeCl}_2 + \frac{1}{2}\text{O}_2$	-7.600	-5.200
$\text{MgO} + \text{Cl}_2 = \text{MgCl}_2 + \frac{1}{2}\text{O}_2$	+4.000	+6.200
$\frac{1}{3}\text{Cr}_2\text{O}_3 + \text{Cl}_2 = \frac{2}{3}\text{CrCl}_3 + \frac{1}{2}\text{O}_2$	+14.360	+18.600
$\frac{1}{2}\text{TiO}_2 + \text{Cl}_2 = \frac{1}{2}\text{TiCl}_4 + \frac{1}{2}\text{O}_2$	+19.000	+15.900
$\frac{1}{3}\text{Al}_2\text{O}_3 + \text{Cl}_2 = \frac{2}{3}\text{AlCl}_3 + \frac{1}{2}\text{O}_2$	—	+9.400
$\frac{1}{2}\text{SiO}_2 + \text{Cl}_2 = \frac{1}{2}\text{SiCl}_4 + \frac{1}{2}\text{O}_2$	+24.300	+21.400

Variation of free energy during reaction of oxides with hydrogen chloride /44/

Table 86

Type of reaction	Variation of free energy at different temperatures, in kcal	
	500°	1000°
$\text{Ag}_2\text{O} + 2\text{HCl} = 2\text{AgCl} + \text{H}_2\text{O}$	-47.800	—
$\text{PbO} + 2\text{HCl} = \text{PbCl}_2 + \text{H}_2\text{O}$	-25.700	-18.400
$\text{CdO} + 2\text{HCl} = \text{CdCl}_2 + \text{H}_2\text{O}$	-22.800	-16.100
$\text{Cu}_2\text{O} + 2\text{HCl} = 2\text{CuCl} + \text{H}_2\text{O}$	-16.600	-5.900
$\text{MnO} + 2\text{HCl} = \text{MnCl}_2 + \text{H}_2\text{O}$	-13.900	-3.300
$\text{NiO} + 2\text{HCl} = \text{NiCl}_2 + \text{H}_2\text{O}$	-10.800	+200
$\text{ZnO} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2\text{O}$	-10.500	-11.000
$\text{SnO} + 2\text{HCl} = \text{SnCl}_2 + \text{H}_2\text{O}$	-10.100	-10.000
$\text{FeO} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{O}$	-9.200	+1.400
$\text{MgO} + 2\text{HCl} = \text{MgCl}_2 + \text{H}_2\text{O}$	+2.400	+12.800
$\frac{1}{3}\text{Cr}_2\text{O}_3 + 2\text{HCl} = \frac{2}{3}\text{CrCl}_3 + \text{H}_2\text{O}$	+12.700	+25.200
$\frac{1}{2}\text{TiO}_2 + 2\text{HCl} = \frac{1}{2}\text{TiCl}_4 + \text{H}_2\text{O}$	+17.400	+22.500
$\frac{1}{3}\text{Al}_2\text{O}_3 + 2\text{HCl} = \frac{2}{3}\text{AlCl}_3 + \text{H}_2\text{O}$	—	+16.000
$\frac{1}{2}\text{SiO}_2 + 2\text{HCl} = \frac{1}{2}\text{SiCl}_4 + \text{H}_2\text{O}$	+22.700	+28.000

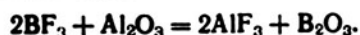
As shown by Tables 85-87, among the possible reducing agents of oxides (chlorine, hydrogen chloride and fluorine) fluorine has the relatively greatest intensity; so, for instance, oxides like MgO , Cr_2O_3 , Al_2O_3 , TiO_2 , or SiO_2 may be reduced by fluorine at a gas pressure of 1 atm, whereas the same oxides cannot be reduced by chlorine and hydrogen chloride at the same pressure.

Variation of free energy during reaction of
oxides with fluorine /44/

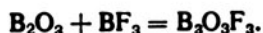
Table 87

Type of reaction	Variation of free energy at different temperatures, in kcal		
	25°	500°	1000°
$\frac{1}{2}\text{TiO}_2 + \text{F}_2 = \frac{1}{2}\text{TiF}_4 + \frac{1}{2}\text{O}_2 \dots$	- 72.6	—	—
$\frac{1}{3}\text{Al}_2\text{O}_3 + \text{F}_2 = \frac{2}{3}\text{AlF}_3 + \frac{1}{2}\text{O}_2 \dots$	- 74.2	- 67.0	- 59.9
$\text{Cu}_2\text{O} + \text{F}_2 = 2\text{CuF} + \frac{1}{2}\text{O}_2 \dots$	- 75.0	- 68.0	- 63.7
$\frac{1}{2}\text{SiO}_2 + \text{F}_2 = \frac{1}{2}\text{SiF}_4 + \frac{1}{2}\text{O}_2 \dots$	- 72.0	- 84.4	- 86.9
$\frac{1}{3}\text{Cr}_2\text{O}_3 + \text{F}_2 = \frac{2}{3}\text{CrF}_3 + \frac{1}{2}\text{O}_2 \dots$	- 83.6	- 77.0	- 73.1
$\text{Ag}_2\text{O} + \text{F}_2 = 2\text{AgF} + \frac{1}{2}\text{O}_2 \dots$	- 86.2	—	—
$\frac{1}{2}\text{ZrO}_2 + \text{F}_2 = \frac{1}{2}\text{ZrF}_4 + \frac{1}{2}\text{O}_2 \dots$	- 89.0	- 81.6	—
$\text{ZnO} + \text{F}_2 = \text{ZnF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 89.9	- 85.2	—
$\text{MnO} + \text{F}_2 = \text{MnF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 92.0	- 84.7	—
$\text{NiO} + \text{F}_2 = \text{NiF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 94.7	- 88.7	- 83.5
$\text{CoO} + \text{F}_2 = \text{CoF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 97.2	- 89.6	- 82.2
$\text{CdO} + \text{F}_2 = \text{CdF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 97.5	- 95.4	- 94.6
$\text{FeO} + \text{F}_2 = \text{FeF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 100.0	- 90.5	- 81.7
$\text{PbO} + \text{F}_2 = \text{PbF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 103.0	- 96.8	- 90.8
$\text{MgO} + \text{F}_2 = \text{MgF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 112.4	- 103.8	- 96.6
$\text{CaO} + \text{F}_2 = \text{CaF}_2 + \frac{1}{2}\text{O}_2 \dots$	- 133.3	- 125.5	- 118.4

Boron fluoride reacts with many oxides, promoting their decomposition. Among them, particularly aluminum oxide reacts with boron fluoride at 450° C, according to the equation

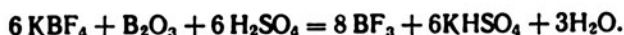


Aluminum fluoride is a volatile substance. Boron anhydride, with an excess of boron fluoride, reacts with the latter, according to



The product of this reaction is volatile but upon cooling it decomposes forming a solid precipitate of $\text{B}_2\text{O}_3 \cdot h\text{BF}_3$ ($\frac{1}{2} > h > \frac{1}{3}$) /45/.

Boron fluoride used for soldering purposes may be obtained by heating boron anhydride (B_2O_3) and potassium fluoborate (KBF_4) in sulfuric acid up to a temperature of about 150-200° C. This occurs according to the following reaction /46/:



All the components of this solution should be in a chemically pure form. The solution is to be prepared in a glass flask first dissolving in sulphuric acid, boron anhydride (B_2O_3) and then gradually adding potassium fluoborate (KBF_4). The flask then is sealed e.g. with a plastic plug through which a glass or stainless tube projects. The flask is heated in an electric stove permitting adjustment of the heat intensity. Figure 135 shows a diagrammatic representation of a laboratory unit* for preparation of boron

* This laboratory unit has been devised and tried by D.M. Dubrovskii, A.M. Polyakov, and A.S. Bolovinov.

fluoride. Prior to soldering, the container is purged for 20-30 min with a jet of nitrogen carefully dried and cleaned by passage through "Tishchenko" bottles filled with concentrated nitric acid, and through copper cuttings heated up to 700°C. During this operation, the reaction flasks for preparation of boron fluoride should be disconnected since nitrogen is furnished under pressure. Boron fluoride may also be obtained by heating up to several hundreds of grades /46/ fluoborates (e.g. NaBF_4 , KBF_4 , $\text{Na}_3\text{PO}_4 \cdot 3\text{BF}_4$, $\text{K}_3\text{PO}_4 \cdot 3\text{BF}_3$, etc) which, when heated decompose to metallic fluorides and boron fluoride /46/.

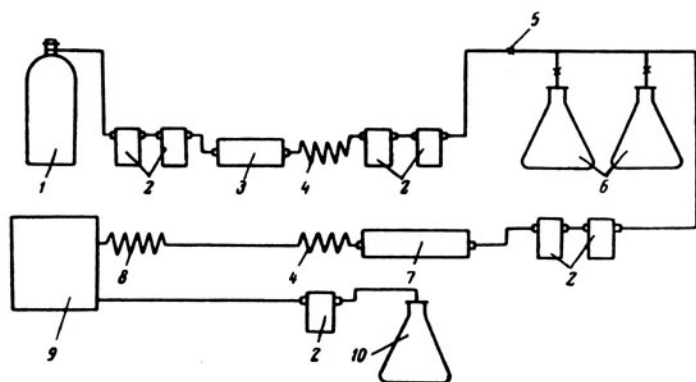


Figure 135. Diagrammatic representation of a laboratory unit for preparation of boron fluoride (BF_3):

1—nitrogen bottle; 2—Tishchenko bottles; 3—furnace with copper cuttings heated up to 700°C; 4—cooling coil; 5—connecting cocks; 6—retort for preparation of BF_3 ; 7—furnace with steel cuttings heated up to 900°C; 8—coil for gas heating; 9—container for soldering; 10—flask with acetic acid.

Boron fluoride is a gaseous substance which boils at 101°C and melts at 128.7°C; it is heavier than air and at 130°C its specific gravity is 1.87 g/cm³.

After ceasing to purge the system with a nitrogen jet, the system is filled with boron fluoride subjected prior to its introduction into the container to a careful drying in 2-3 Tishchenko bottles and in a furnace filled with steel cuttings, heated to 900°C. Evolution of boron fluoride should be quiet (without violence), and may be adjusted by proper heating (in an electric stove).

After passage through the container, the gas is conveyed through a control Tishchenko bottle for checking the degree of impurification of the container, and then transferred into a flask with acetic acid for neutralization. Heating of the container for subsequent soldering may be done only after thorough purging with a stream of boron fluoride.

The unit should operate under an extraction hood equipped with flaps, which are permanently closed until the completion of the process. Gas residues are removed from the container by a dry nitrogen jet. Sometimes the parts are washed in aqueous solution of soda.

In soldering 40KhMA steel parts with PSr40 solders and a Cu + 15% Mn alloy, it has been found that boron fluoride when using copper-manganese solders has a particular activity at a soldering temperature above 1000°C. In such cases soldering may be accomplished also with poorly cleaned gases. On the other hand, soldering parts with PSr40 solders at a temperature below 1000°C (i.e. at 650-700°C) requires a particular careful removal of moisture from the fluxing substance.

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* [Translator's note: Direct reproduction of Latin text as quoted in Russian original].

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Chapter XVI

REACTION AND DIFFUSION SOLDERING

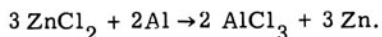
§ 1. Chemical Reduction of the Solder During Soldering

Reaction-soldering is essentially a process of joining achieved by means of solders which form as a result of a chemical reaction during soldering. Though known for a long time, reaction-soldering methods are still in the very beginning of their development.

At present, three kinds of reaction-soldering processes, differing in the method of formation of the solder, may be distinguished; reduction of the solder from metallic salts (fluxes); evaporation of the volatile components of the solder or flux, and contact-reaction soldering in which a low-melting liquid solder forms on the interface between the parts to be soldered. Two or three of these methods may be combined to suit various soldering techniques. The first and third of these methods are termed self-fluxing (or fluxless) soldering methods.

The first method (reduction of solder from metallic salts), is applied mainly in the soldering of aluminum parts (described in several German patents from the end of the last century). According to these patents, chlorides, bromides or iodides of certain heavy metals, or mixtures of these compounds may be used as reaction agents; such substances are e.g. the chlorides, iodides and silver bromides; mixtures of sodium and zinc chlorides, zinc chlorides, ammonium bromides, sodium fluorides, etc. Metals or alloys, reduced from these metallic salts have a relatively high melting point.

The reduction process may clearly be visualized if considering the example of soldering aluminum with zinc chlorides which occurs according to the reaction



The aluminum chloride vapor formed during that reaction, volatilizes. Zinc reduced in the course of this reaction (at a temperature of 419°C), melts and flows into the gap between the parts.

Reduction of tin, lead, antimony, cadmium, silver or bismuth from their chlorides occurs in the same way. Silver forms with aluminum a eutectic which melts at 558°C .

Reaction-soldering mixtures containing ZnCl_2 or SnCl_2 , though known

long before /1/, gained widest acceptance only after the paper of Neubauer-Nicolini was published /2/.

In the meantime, several reaction mixtures for soldering of aluminum were devised; in the course of soldering these substances promote reduction of tin, zinc, or of the zinc-tin alloy (see Table 88).

Table 88

Reaction mixtures for soldering aluminum /2/

Composition of the mixture, %					Temperature of reduction of the metal, °C
ZnCl ₂	SnCl ₂	NH ₄ Br	NH ₄ Cl	NaF	
90	—	8	—	2	420
90	—	—	8	2	380
—	90	—	8	2	330
90	—	—	10	—	410
—	90	—	10	—	360
45	45	—	10	—	330
76.5	13.5	8	—	2	380
76.5	13.5	—	8	2	370
72	18.0	8	—	2	350
72	18	—	8	2	340
46.8	43.2	8	—	2	330
46.8	43.2	—	8	2	320

In practice, joining is done by this method in the following manner: the seam area is covered with a pasty reaction mixture. In order to avoid overheating of the mixture, the joint is heated so as to prevent direct contact of the mixture by the heating flame. After formation of aluminum chloride vapors, of liquid metal, and of the solder, the latter flows into the gap between the parts; the joint is then cooled and the residues of the reaction mixture are washed off.

Reaction-soldering mixtures containing NH₄Cl have a series of advantages as compared with mixtures composed of NH₄Br. By replacing ZnCl₂ with SnCl₂ the temperature of reduction of the metal may be lowered. The hygroscopicity of reaction mixtures (or self-fluxing solders) containing SnCl₂ is smaller than that of mixtures containing ZnCl₂.

Zinc or tin, reduced during the soldering process, combines with aluminum to form a series of intermediate alloys, according to the equilibrium diagram of Al—Sn or Al—Zn. Apart from this, zinc and tin tend to diffuse along the grain boundaries of aluminum.

In the course of soldering, the fused salts partially dissolve aluminum or its alloys and disturb the bond between aluminum oxides and the surface of the base metal. AlCl₃ vapor and some other volatile compounds destroy the oxide film which floats to the surface of the molten zinc or tin. Fluoride self-fluxing mixtures partially dissolve aluminum oxides.

Since the specific temperature of soldering with reaction-mixtures causes a certain softening of aluminum and its alloys as a result of re-aging or relieving from cold-hardening stresses, the mechanical (ultimate) strength

of joints soldered with these substances is rather small. So, for instance, the ultimate strength of lap-joined aluminum sheets varies from 9.0 to 9.5 kg/mm²; failure occurs in the base metal. In resistant lap-joined aluminum alloys, failure occurs in the soldered seam (due to the reduced mechanical strength of the solder); the strength of such a joint varies from 11 to 16 kg/mm².

Reaction soldering has been applied in joining aluminum-core cables to their cable shoes /3, 4/.

Soldering is done in the following way. The preliminarily cleaned parts are covered with a pasty reaction-mixture and then subjected to heating. Proper heating insures proper joining of the shoes to the cable and removal of gaseous residues of the reaction mixture. One disadvantage of this method is the difficulty in checking the quality of the soldered joint. Its merit lies in the rather uncomplicated soldering technique involved (since no intricate appliances or equipment are needed).

Reaction-soldering mixtures may be combined with an appropriate solder. This method has been applied particularly in the joining of cable shoes to aluminum cables /5/. The reaction-mixture used for this purpose was prepared on the base of SnCl₂ and had a melting point of 193°C; its activity started at a temperature of 360°C. In the course of reduction, the surface of the parts to be soldered was covered with a liquid oxide film reacting with the solder, while the aluminum chloride vapor volatilized. For soldering, two alloys composed of 1) 70 % Zn + 30 % Sn and 2) 95 % Zn + 5 % Al have been used.

Joining of the cable was done by dipping in the molten solder at a temperature of 400°C. Prior to soldering, the cable was covered with the reaction mixture and then dipped in the molten solder.

The method of combining reaction mixtures with solders is suitable for torch, furnace or dip-soldering. There are several methods of dip-soldering. Besides the method stated above, dip-soldering may be done in two steps: 1) Dipping in molten flux, at 230°C; 2) Dipping in molten solder. The bath temperature of the first solder is 400°C, of the second, 425°C.

The reaction method (by reduction of metallic oxides) may be used also in joining metals to ceramics (e.g. reduction of Mo from MoO₃).

The second method consists in applying chemical compounds, the constituents of which are able to volatilize during heating. Sometimes, the non-volatile metallic constituents of the substance, combined with other metals, may be used as solders. These volatile constituents form a protective blanket against oxidation of the seam. At present, similar soldering methods are still in the development stages. Such substances used in soldering at present which decompose upon heating, are hydrides of certain metals, (zirconium, titanium, niobium or tantalum), from which hydrogen is previously removed.

§ 2. Contact-Reaction Soldering

Contact-reaction soldering is based on the fact that dissimilar solid metals or alloys, while in mutual contact and heated below their melting point, are able to melt to a definite depth of the metal layer. This partial melting (fusion) of contacting solid metals or alloys may be achieved by heating such metals that form eutectics or a continuous series of solid

solutions with a minimum melting point (e.g. copper with gold). Certain contacting alloys, while heated, may form a ternary or quaternary eutectics /6, 7/. The liquid alloy layer formed on the interface between the parts constitutes the solder which, upon solidification, assures the junction of two or more dissimilar metals or alloys. This method of joining is sometimes termed self-soldering.

The contact-reaction method has been applied for a long time in the soldering of gold or silver decorative or ornamental work. It permits a great diversity of procedures: such as (a) soldering of two metals or alloys forming a binary or multicomponent eutectic; (b) soldering of similar or dissimilar metals which do not form eutectic structures between them but do so with another metal or alloy which, in this case, is inserted in the shape of a foil, between the members of the joint; (c) electroplating or metal cladding.

Thanks to the presence of a eutectic in the binary Al-Cu system, with a content of 33% Cu at 548°C, the contact-reaction method may be employed in soldering aluminum to copper. Butt-soldering of two rods presents only technical difficulties. The Al-Al₂Cu eutectic formed through contact between Al and Cu heated over a range from 548° to 660°C has a certain brittleness; the thicker the eutectic layer, the less plastic is the soldered joint. Due to formation of a brittle eutectic layer during contact soldering of Al to Cu, butt welding of these metals is also limited /8/. Another obstacle in the use of contact-soldering of aluminum to copper may arise from the formation of swellings (flashes) on the soldered joint as a result of the contact-reaction-process. A simple method of contact-reaction soldering of aluminum to copper has been advanced which avoids formation of flashes and of a thick eutectic layer /9/. To join such metals, the aluminum rod is placed in a lower position in the inner guiding cylinder of the heating furnace. The flat pointed front end of the rod touches the copper rod to be joined. After heating the place of contact between both rods, above the temperature of formation of the Al-Al₂Cu eutectic, (548°C), but below the melting point of aluminum (660°C), the conical end of the copper rod is driven by striking or by means of a press, into the aluminum rod. In the course of pressing, a eutectic is formed which, upon cooling, assures a rigid bond between both rods. Any excess of liquid eutectic and oxide film is removed during pressing in of the copper rod. The tensile strength of such a joint equals that of the aluminum proper. This method may be applied for the soldering of two metals forming eutectics which present considerable differences in the hardness and melting point. Of course, the metallic rod which has the greater hardness and a higher melting point, must be given a pointed end required for driving it into the other rod with which it is to be joined.

The contact-reaction method with a metallic interlayer has been used in the soldering of silver to aluminum alloys. Prior to joining, the parts are properly prepared and the gap between them is filled with a silver foil 0.05-0.12 mm thick. The parts are then subjected to a pressure varying from 70 to 350 kg/cm². Next, they are heated by means of an oxy-acetylene torch or in the induction furnace, at a temperature above the melting point of the Al-Ag eutectic (558°C). By this method the ultimate strength of aluminum alloys soldered reaches ~ 21 kg/mm² /10/.

In the soldering of coolers, sometimes copper sheets clad with a thin silver layer (0.006 mm thick) may be successfully used. At a temperature of 778°C copper forms with silver a eutectic structure. Contact-reaction

soldering of metal-clad copper-sheet coolers is done at a temperature of 800°C without fluxing agents, in a reducing furnace filled with dissociated ammonia gas.

As a result of heating, at the interface of the metal-clad copper strips, a thin eutectic interlayer is formed composed of 71% Ag and 29% Cu. Formation of a eutectic is preceded by mutual interdiffusion of copper and silver to their saturation limit (copper dissolves up to 8% Ag, whereas silver 8.8% Cu). The thickness of the copper strips was 0.2 mm.

Furnace-soldering of thin brass guide-waves can be easily effected by the prior application of a thin silver layer (0.006–0.012 mm). Between the brass parts electroplated with a thin silver blanket and heated up to 682°C, a liquid layer of ternary alloy containing 60% Ag, 15% Cu and 25% Zn, is formed. In order to eliminate formation of such a liquid interlayer, heating up to 700°C is applied [11]. Heating is accompanied by a process of interdiffusion of silver into brass and copper and zinc into silver; after the alloying elements reach the above stated degree of concentration, liquid eutectic is formed. The liquid condition of this low melting eutectic favors its diffusion into the solid metal of the members of the joint; after solidification, the low melting alloys proved to be rigidly bound to the brass parts.

Contact-reaction soldering may be carried out not only between metals that form eutectics or continuous series of solid solutions with a minimum melting point, but also between multicomponent alloys on the interface of which a multicomponent eutectic (of the ternary or quaternary system) is liable to be formed.

This possibility can be realized by the example of contact-soldering of multicomponent alloys [7]. Such a phenomenon could be noticed also during contact-joining of organic substances forming a eutectic structure [12].

In order to study the contact-reaction soldering of Al–Si alloys, special investigations have been carried out by the authors of the present study. Contact-reaction soldering of these alloys has been accomplished at a temperature of 535°C with solders containing 1–7% silicon and copper. As it was found, the soldering time depends on the content of the components of the alloy in contact: the higher the concentration of the alloying components (within the limits used in the course of these investigations) in the alloys to be joined, the faster formation of a low-melting multicomponent eutectic structure, which fills the gap between the parts to be soldered, occurs.

Heating of the contacting alloys leads to the formation of a ternary Al–Si–Cu eutectic having a melting point of 525°C.

The contact time of this soldering process is governed by the rate of diffusion between the soldered alloys.

Soldering occurs in three stages. The first stage is marked by diffusion in the solid condition. The portions close to the contact area are saturated with alloying elements in a concentration sufficient to form a eutectic structure.

In the second stage those portions of the alloy having a eutectic structure are molten. The liquid phase thus formed promotes further diffusion of alloying components, thus leading to a gradual increase in the thickness of the eutectic interlayer. After discontinuing heating of the contacting alloys, the soldering process enters the third and last stage—solidification.

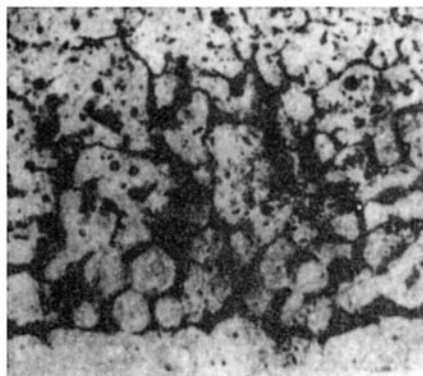


Figure 136. Microstructure of a test specimen taken from a cast-aluminum alloy containing 5% Si and joined by the contact-reaction soldering method with a deformed 1% Cu-Al alloy. Enlarging $\times 130$

Soldering of the previously stated Al-Si alloy to the Al-Cu alloy at temperatures above the melting point of the eutectic occurs by formation of a continuous liquid interlayer, or of a liquid low-melting eutectic developed along the grain-boundaries of one of the contacting alloys. The first way is achieved chiefly in soldering of hot worked alloys, the other in the soldering of cast alloys.

The liquid frontal layer or the liquid boundary layer forms in the aluminum silicon member of the joint, since copper has a considerably greater diffusion rate than silicon. Figure 136 illustrates the structure of a cast 5% Si-Al alloy test-specimen, soldered to a 1% Cu-Al deformed test-specimen on the interface between the metals. The microphoto clearly reveals the layer of recrystallized alloy advanced in the Al-Si layer, and the ternary Al-Cu-Si eutectic developed along the grain boundaries. Figure 137 shows in a big enlargement the structure of the ternary eutectic developed along the grain boundaries. The structure of a seam resulting from soldering a 7% Si aluminum-alloy specimen to a 3% Cu aluminum-alloy specimen, is shown in Figure 138.

During these investigations, diffusion of copper into the Si-Al alloy did not proceed uniformly from the point of contact, but developed with a greater velocity along the grain boundaries. The grains of the Al-Si alloy where copper atoms diffused, showed a lower solubility of silicon: being less dissolved it appears here in greater quantities than in the base metal. Along the grain boundaries, separations of ternary eutectic can be noticed: due to this fact, portions close to the grain boundaries are impoverished in alloying elements. Such layers of homogenous solid solutions propagate into the mass of the Al-Si alloy together with the ternary eutectic separated along the grain boundaries.

Reaction-contact soldering is achieved at a certain pressure required for a tight contact and better diffusion, and for relieving contraction stresses upon freezing of the liquid interlayer.

Titanium may be successfully soldered with high-copper silver solders at a temperature below the melting point of the solders involved [13]. Apparently, in this case a eutectic is formed between titanium and the alloying components of the solder.



Figure 137. Structure of the ternary eutectic in the contact joint shown in Figure 132. Enlarged X350

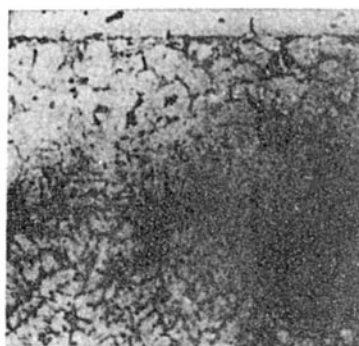


Figure 138. Microstructure of a joint obtained by contact soldering of a deformed 5% Cu—Al alloy test specimen to a 7% Si—Al cast alloy test specimen. Enlarged by X130

§ 3. Diffusion Soldering

As a rule, different portions of the soldered joint, due to the high soldering rate and to the rapid cooling of the molten metal in the gap between the parts, exhibit a disturbed physicochemical equilibrium both during and after soldering. Prolonged heating of the soldered seam during or after soldering is liable to cause essential changes in the structure and properties of the soldered joint, connected with the relative equalizing of composition and structure of the soldered seam due to diffusion processes.

In certain instances, e.g. in furnace-soldering and particularly in vacuum soldering, conditions may arise which favor a relative state of equilibrium in the soldered seam.

Such soldering methods, as distinct from customary rapid soldering procedures, we may term diffusion soldering.

Diffusion soldering is based on certain advantages of the internal structure created as a result: 1) of an equilibrium between the molten solder and the base metal or alloy established at high temperatures; 2) after reaching a state of equilibrium at a temperature below the soldering temperature proper; 3) after reaching a relative equilibrium in the soldered seam at the soldering temperature and upon subsequent homogenizing at lower temperatures.

In the following, certain simple though essential instances of diffusion soldering may be considered.

In the authors' view, particularly promising seem to be instances of diffusion soldering where, as a result of homogenizing at soldering temperature, the liquid phase (of molten solder) disappears, since upon solidification of the latter, non-equilibrium structures may form which cause embrittlement of the soldered seam.

So, for instance, when using solders, the components of which form a continuous series of solid solutions (equilibrium diagram of lenticular form), homogenization of the alloy associated with annihilation of the liquid phase may take place. Such instances may be encountered when soldering copper to nickel.

In fast soldering, the soldered seam consists of three layers: 1) base metal; 2) solidified solder; 3) base metal. In diffusion soldering the resultant joint exhibits a single phase, and its different portions are formed of a solid solution with different concentration of alloying elements.

In customary (fast) soldering, the solder upon crystallization forms an interlayer between the parts to be joined, whereas in diffusion-soldering this interlayer disappears as a result of the homogenizing process; the soldered seam has a single phase. Such a seam is always more plastic than a multiphase seam and its mechanical strength is often greater. Similar processes occur at elevated temperatures and in slow soldering of nickel alloys by means of a very thin layer of a eutectic Ni-P solder (obtained e.g. from hypophosphite solutions used in chemical nickel coating).

Diffusion soldering may be useful in the joining of high alloyed metals (e.g. in soldering heat and oxidation resistant (thermostable) alloys), with low-alloyed solders.

At elevated temperatures when the diffusive mobility of metallic atoms is particularly high, alloying elements from the base metal diffuse into the solder interlayer. Due to this fact, the strength of the solder interlayer may become as high as the strength of the base metal. This method is particularly practicable in cases where, after soldering of alloys containing chromium, aluminum or silicon, strong oxide films form on the surface of the soldered seam, which should be removed. Solder without such elements or including them in a reduced amount may be used also as a coating to protect the base metal from oxidation during soldering.

Diffusion soldering of thermostable nickel- and iron-base alloys is done with nickel solders containing a large amount of manganese which forms solid solutions with nickel and has a reducing effect on the melting point of the solder.

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Chapter XVII

BRAZE WELDING

Braze welding* is a variety of the brazing process in which permanent joints similar to welded joints may be obtained (Figure 139) by means of a filler metal, but unlike welding, without the base metal being molten.

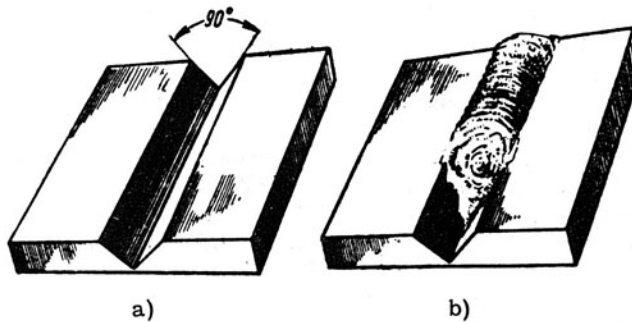


Figure 139. Preparation (beveling) of edges of plates prior to braze welding (a), and the gap between the plates (b) partially filled with molten metal during braze welding

Filling of the gap with molten metal occurs mainly due to forces of gravity, without any practical interference of capillary forces.

In the twenties of the present century, braze welding was initially employed for soldering steel and cast iron with brass solders. Throughout the following years, the soldering technique, essentially remained unchanged, being mainly used for soldering of cast iron and aluminum parts. Braze welding of aluminum and its alloys is made with a silumin filler-metal.

Braze welding is carried out with an oxy-acetylene torch or by the electric-arc welding methods /1/-/14/.

* [Translator's note: Braze welding is a synonym for "bronze welding" or "bronze brazing" but the first term corresponds better to the real meaning of the process].

In the joining of cast iron, braze welding has a broader field of application than the conventional capillary soldering, as it is more easily achievable than customary soldering. The main advantage of braze-welding cast iron as compared with welding lies in the greater plasticity of the resulting joint, since during welding cast iron is liable to melt and to form a brittle chilled layer on the seam upon solidification.

Braze welding of cast iron is applied both for permanent uniting of parts and for repairing cracks or other defects.

The use of braze welding mainly for cast iron parts is understandable, since both strength of the seam and of the base metal (cast iron) have similar values whereas the strengths of steel and the brass seam resulting from braze welding greatly differ. The strength of a braze-welded joint is determined by the strength of the seam. Strength of test specimens taken from a soldered seam is $\sim 20 \text{ kg/mm}^2$.

The filler rod (metal) used in braze welding of cast iron contains brass with 58–62% Cu. In the cast condition, this brass consists of two phases ($\alpha + \beta$) and does not exhibit hot brittleness as the α -brass does. Brass of such a composition solidifies at a temperature of about 900°C and has a limited crystallization range; both these factors greatly favor solidification of the soldered seam. Addition of tin, nickel, iron, manganese or silicon to the filler metal yields increased strength of the welding metal and of the resulting joint as well. Lead-bearing brass filler proved to be unsuitable since it causes porosity of the seam. Originally, filler metals of Tobin bronze (57–62% Cu, 38–41% Zn, 1% Sn, 1% Fe and 0.8% Mn) were usually used, due to the favorable effect of tin on the fluidity of the filler metal, and also owing to the strengthening effect of iron and manganese on the bond with the base metal and on the resulting joint. Silicon added to brass fillers functions as a deoxidizer of zinc, strengthens the filler metal and reduces the porosity of the soldered seam.

Brass filler metals containing about 1% Ag, the S18-chastolin alloy containing 58% Cu, 41% Zn and 1% Ag, and the S16-chastolin alloy composed of 46% Cu, 8% Ni, 45% Zn and 1% Ag are also recommendable for filler metals /14/.

Of great importance in braze welding is the preparation of the surface, and particularly, the removal of graphite from the surface of cast iron parts. Removal of graphite is done by oxidation: 1) with a paste of steel cuttings, with boron anhydride or with calcinated borax both of which upon heating evolve hydrogen which forms with graphite a volatile carbonate gas; 2) through the flame of the welding torch at an excess of oxygen. The small capillaries formed in cast iron during burning of graphite are filled with the filler metal and constitute an additional bonding medium for the base metal of the joint.

The edges of the joint are V-shaped (less frequently X-shaped). To improve adherence of the iron edges to the filler metal, the grooves of the joint are roughened or sometimes channeled. Preferably, the bevel angle should be 90° .

Prior to braze welding, the surfaces of the cast iron edges should be pretinned without using any flux. For this to be done, the edges are heated up to $800\text{--}900^\circ\text{C}$; the filler metal heated in the torch flame is moved over the edges and rubbed so that a tinned layer is deposited on the surface of the edges. No visible diffusion of the filler metal into the cast iron base metal is noticed during braze welding operations.

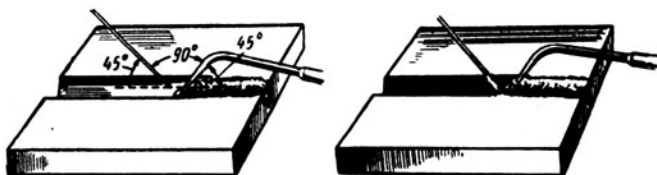


Figure 140. Position of filler metal and brazing torch with respect to the edges of the joint during braze welding

The flame of the oxy-acetylene torch used in braze welding is neutralizing, though according to some authorities [8], an excess of acetylene or oxygen is liable to reduce the quality of the soldered seam, whereas, on the contrary, some researchers affirm that a small excess of oxygen may be useful [3, 6] or even necessary [11].

Figure 140 shows the approximate position of the filler metal, of the brazing torch, and of the edges of cast iron parts. Prior to soldering, irregularly shaped or heavy parts are preheated up to 300-400°C. Fluxing is done with a mixture of borax and boron anhydride (mixing ratio 1:1). After the molten metal has filled the gap between the parts, the seam should be kept for a certain time in the liquid state, to ensure removal of gases. In order to avoid formation of cracks, the soldered parts should be cooled slowly (in sand, in a furnace, etc.) Heating of cast iron after braze welding for 15-20 min in the range from 750° to 800°C, favors increase in strength of gray cast iron. The strength of a braze-welded seam depends on the grade of the brass filler used in the process. The ultimate strength of a seam braze-welded with an L62 brass filler varies from 20 to 26 kg/mm² [81]. The ultimate strength of the seam soldered by special brasses, may be equal to 29 kg/mm² and when soldered by Tobin-bronze to about 33 kg/mm². If using a silicon bronze the strength may be increased (up to 38-40 kg/mm²); Brinell hardness of such seams varies from 70 to 100 kg/mm².

The melting point of brass filler used in braze welding of malleable iron should not exceed the temperature of dissolution of the annealing carbon (950-1040°C). The melting point of the solder (filler) should not exceed ~900°C [4].

In the following an example of braze welding for building up cracks in cast iron parts, may be considered [9]. As a preliminary operation, the place where the crack occurred is to be cut around from one side at an angle of 60-90°, leaving an unchamfered edge (rootface) of about 20% from the thickness of the work. During brazing, the torch should be kept at an angle of ≤ 10°, otherwise splashing of the liquid filler metal, burning of zinc, or porosity of the seam is likely to occur. The opposite sides of the edges should be smeared with a fluxing substance. Preheating of the edges should be done with a stronger flame (a torch with a larger nozzle number) than that which is customarily applied in the soldering technique.

Braze welding of cast iron parts with brass fillers may be done either in the vertical or in the overhead position [13, 14]. Brazing is done by means of a gas torch. Preparatory steps for braze welding are the following: V-shape beveling, (customary in braze welding); removal of dirt, grease, oxides, and rough spots (by channeling with a chisel). Prior to braze welding,

the work is to be pretinned and then preheated up to 300–400°C. The flame cone should be kept at a distance of 8–10 mm from the surface of the melting metal added.

When cast iron is braze welded in a vertical position, the molten metal bath is kept from flowing out by the pressure of the gas flame. Vertical braze welding of cast iron is done by successively depositing thin layers of rapidly freezing molten metal.

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Chapter XVIII

QUALITY CONTROL OF SOLDERED JOINTS

Choice of the design of a soldered joint, the proper solder and flux (if required), and the soldering technique, though of great importance in obtaining sound soldered joints, do not always ensure the required quality, since soldering of individual components of a work cannot be done with the proper accuracy. This also applies to automatic soldering without a man's direct interference and still more to soldering processes where manual operations are essential.

The capillary type of soldering is a rather fast process; the basic phenomena and processes which are decisive factors in the soldering occur in the invisible capillary space between the members of the joint, inaccessible for direct inspection during soldering; only the ready soldered joint permits a direct control and examination.

Requirements the quality of a soldered joint has to meet with depend on the working conditions of the joint. Soldered parts operating under static load and vibrations or subjected to impact, short-time or prolonged stresses, should be able to withstand them without failure at given maximum stresses and temperatures.

Parts subjected in the course of their service to hydrostatic or gas pressure should be hermetic and should have sufficient mechanical strength. /1/.

Soldered current-carrying components of electrical equipment and devices should possess the required degree of electric conductivity, etc.

Soldered parts must have sufficient corrosion-resistance.

The best method for testing the quality of a soldered point is to check its working capacity in operating conditions over a given period. Yet, for different reasons, such an inspection cannot always be carried out. In a series of instances, production trials require much time, and therefore in the quality control of soldered joints, such methods are applied which permit estimation of the working capacity without resorting to production tests.

Sometimes production tests are replaced by laboratory tests reproducing or simulating the true working conditions of the soldered joint. Such methods are bound to give direct results whereas other methods permit only an indirect judgement upon the working capacity of soldered joints /2/.

Inspection methods may be devised in two groups: quantitative and qualitative methods. The first group covers methods which enable us to obtain data on the working capacity of a given soldered joint (e.g. testing of

mechanical strength, plasticity, tightness, electric conductivity etc.) Qualitative methods are based on the results of long time observation and comparison of characteristics of the given joint, the extent of filling the gap with solder metal, and of different defects and working capacity of the soldered joints.

There are destructive and non-destructive methods of testing. Non-destructive methods consist in the detection of different defects and revealing their danger for the soldered joint. Table 89 presents a synoptic view of certain defects due to incorrect soldering technique in soldered joints, as well as the specific causes which clearly indicate the way for removal.

In certain cases (e.g. large or irregularly shaped parts, scarcity of metal involved, or high cost of the parts), not only the ready soldered joint but also the different stages of its production (routine inspection) should be checked. This implies also a careful inspection of such technological operations as: preparation of surface, maintenance of gap and clamping throughout assembling and soldering, filling of the gap with flux and solder, complying with heating conditions, removal of flux residues after soldering etc.

Tight filling of the gap between the parts with molten solder is of great importance for a sound soldered joint. Quality of filling may be assessed by X-ray examinations, fluorescent or radioactive methods, as well as by visual destructive inspection of test specimens.

The quality of the soldered seam (i.e. tightness of filling of the gap with solder) may be determined also by abrasive testing, by non-destructive X-ray examinations, or by radiographic methods. Usually a 20% non-fusion of the soldered seam is admissible.

Table 89

Typical defects of soldered joints

Type of defect	Causes
Poor spreadability of the molten solder. Poor filling of the gap. Incompletely filled portions of the gap	<ol style="list-style-type: none"> 1. Incorrect design of the soldered joint or bad assembling (small clearance, misalignment of the members of the joint during assembling) 2. Poor preliminary preparation of the surface 3. Incorrect fluxing of the parts during soldering (low-active flux, non-filling of the gap with flux, great differences in the melting point of flux and solder) 4. Insufficient heating of the parts to be soldered
Unilateral filling of gap with molten solder without formation of a fillet (bead) on the opposite side of the seam	<ol style="list-style-type: none"> 1. Poor capillary flowability of the molten solder for a given material for the work and of the flux 2. Insufficient activity of flux 3. Non-uniform (unilateral) heating

Table 89 (continued)

Type of defect	Causes
Fine pores of the seam metal	<ol style="list-style-type: none"> 1. Inclusion of damp oxides in the seam (due to a poorly prepared surface, and to insufficient fluxing) 2. Evolution of gases from the base metal and the soldered seam 3. Overheating of the seam during soldering
Roughness of the surface of the soldered joint and of the tinned portions	<ol style="list-style-type: none"> 1. Excessive soldering temperature 2. Prolonged holding at the soldering temperature 3. Insufficient amount of flux 4. Coarse-grained solder metal
Inclusions of fluxing substances [in the seam]	<ol style="list-style-type: none"> 1. Too much flux 2. Insufficient amount of solder 3. Incorrect clearance (gap) 4. Inflow of molten metal from both sides of the gap 5. During soldering the flux has been enveloped by running solder 6. Difference in the melting point of flux and solder 7. Specific gravity of flux greater than that of solder 8. Non-uniform heating
Etching of the surface of the soldered seam by molten solder	<ol style="list-style-type: none"> 1. Excessive soldering temperature 2. Prolonged holding time during soldering 3. Strong chemical interaction between solder and base metal
Presence of cracks in the soldered seam	<ol style="list-style-type: none"> 1. Misalignment of the members of the joint during solidification of molten solder 2. Large crystallization range of the solder metal
Cracks in the base metal near the seam area	<ol style="list-style-type: none"> 1. Overheating or burning of the alloy 2. Intense intercrystalline penetration of solder in the base metal 3. Non-uniform heating at a low heat-conductivity of the parts to be soldered 4. Considerable difference in the coefficient of thermal expansion of solder and the low plastic base metal

In order to check quality of a soldered seam in steel or nickel-alloy heavy parts surrounded by a thin-walled lining, the method of heating the parts up to a red heat with subsequent cooling in open air, is sometimes applied. Non-fused portions of the seam appear as dark spots on the red hot surface of the heated work.

Soldered parts which require tightness in operation, should be tested for hydrostatic or air proofness; low-pressure tests may be carried out with air pressure whereas high-pressure tests require use of liquids /1/.

In certain branches of industry the routine quality-inspection has been mechanized. So for instance, in the manufacture of can bodies /3/ their air-tightness is proof tested by an automatic unit on which the can bodies are fixed: during operation of the automatic device, liquid is alternately pressure fed to each of the cans; cans not resisting the pressure are automatically rejected from the station.

After soldering, tinplate milk vessels are proof tested by dipping in water. Occasional leakages are immediately revealed by appearance of water droplets (the so-called "tears").

Soldered seams of radio condensers /4/ may be proof tested by the fluorescent method, irradiating the parts after being heated in a conveyor furnace for 1–2 hours at a temperature of 70–80°C, with special mercury-quartz lamps. Molten vaseline, while seeping through any leakages of the seam, becomes fluorescent in the beam of ultraviolet rays emitted from the lamp.

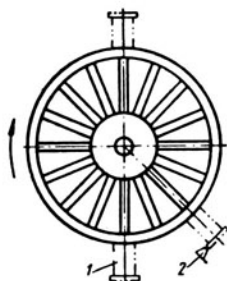


Figure 141. Diagrammatic representation of a unit for proof-testing condenser boxes:

1—position of the charge; 2—adjusting stop.

In another method, the condensers are immersed in an oil exsicator maintained under a vacuum with a residual pressure of 0.14 atm. Air droplets infiltrating through untight places, float to the surface of the oil bath thus revealing location of such leakages.

If soldered parts are immersed in a bath of transformer oil preheated to 110–115°C, the air present in the parts and expanding as a result of heating, appears through the leakages in the body of the work in the form of bubbles. Testing time for medium sized parts is 1 min.

Testing by means of a thermostat is based on the fact, that the condenser filling-medium, while heated up to 70–80°C (for 1–2 hours), expands and floats to the surface of the part leaving oily traces on the filter paper preplaced on the soldered seam.

Proof testing of soldered bodies or boxes may be done on a rotating

station the cover of which is connected to the vacuum line (pipe-line).

In testing, tight parts are pressed on to the rubber cover connected to the vacuum pump due to the pressure difference. Leaky parts are not pressed to the cover while evacuating the air, since the latter penetrates into the parts through existent leakages. These parts drop under their own weight to the bottom of the unit without touching the adjusting stop, while the rest of the parts are ejected from the station, by means of the same stop (Figure 141).

Quality of soldered seams in current-carrying parts, may be checked by measuring their transient resistivity.

The extent of filling the gap with molten solder may be judged by the shape of the fillet on the soldered seam. As a rule, formation of a smooth convex fillet on the soldered seam without sudden transitions in the seam area denotes a good filling of the gap, and obviates overstrains, particularly dangerous if working under alternating loads (stresses). Absence of a smooth fillet denotes either reduced capillary flowability of the molten solder, or strong chemical interaction between the solder and the base metal. In such cases, the so formed sudden transition from the seam to the body of the parts is liable to cause overstressing, if subjecting the parts to peak loads.

Quality control of the tinned layer. This involves inspection of porosity, layer thickness and of strength of bond between the tinned layer and the base metal [5]. Inspection of porosity of the tinned layer is based on the fact that, during interaction of potassium ferricyanide with steel, location of pores is revealed by appearance of (Tornbul) blue spots. For this purpose, the tinned parts are rinsed in gasoline or alcohol and dipped in a warm 5% aqueous solution of H_2SO_4 ; the parts then are rinsed again in water and dipped in a warm solution of 2.5g glycerine, 7.5g gelatin, 1g potassium cyanide to 100 cm^3 of water. Holding time of the work in that solution is 24 hours.

In the quick method of porosity detection based on the same principle, the tinned surface is covered with filter paper previously soaked in a solution of 40 g potassium ferricyanide and 15 g/l sodium sulphate. After 3–5 min, blue spots appear on the porous portions of the work. Porosity of tinplate used in the manufacture of milk vessels, is considered to be within the limits, if the tinned layer has 3 pores on each cm^2 ; a presence of 12 pores on 3 cm^2 denotes medium porosity; more than 12 pores on 1 cm^2 indicates strong porosity.

Thickness of the tinned layer may be determined by weighing test-specimens after their immersion in a 10% solution of NaOH and adding Na_2O_2 , until tin is fully dissolved. Thickness of the tin coating may be computed by means of the following formula:

$$s = \frac{10P}{Sd},$$

where s = layer thickness, mm; S = area of surface of the work, cm^2 ; P = weight of solder, g; d = specific gravity of tin, g/cm^3 .

Strength of bond may be tested by subjecting to a six-fold bending, tinned test-strips at an angle of 90° round a mandrel 1.5 mm in diameter; no cracks or exfoliation in the layer should be present in the test specimen.

Mechanical testing of soldered joints. Suitability of a given solder, flux or soldering technology for the creation of a soldered joint of given mechanical properties, may be tested by means of test specimens soldered

together with the basic joint, or under the same working conditions as the latter. Sometimes, mechanical testing is carried out on test specimens cut from the soldered joint.

Usually, mechanical strength of a soldered joint at room temperature is determined on test specimens composed of two lap or butt soldered pieces (taken from a rod or sheet) (Figures 142 and 143).

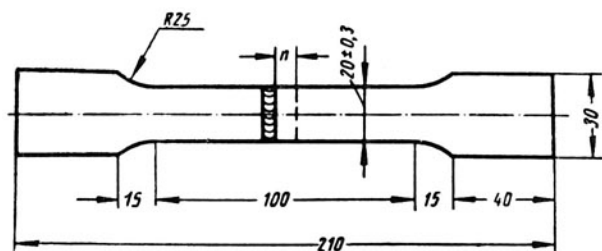


Figure 142. Sketch of a lap-soldered test specimen for testing the shear strength of the soldered joint

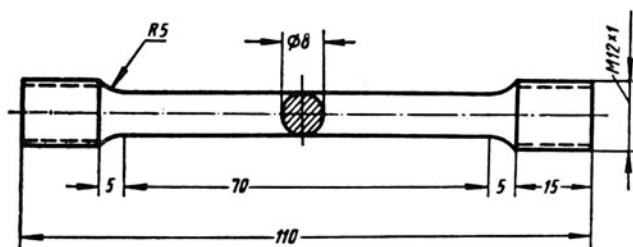


Figure 143. Sketch of a butt-soldered test specimen for testing the tensile strength of a soldered joint

Short or long time testing of soldered joints at elevated temperatures and under vibrating load, as well as creep tests may be carried out on special test specimens provided in the center of their gage length with a butt or lap seam. Testing is done in customary testing machines.

Certain difficulties arise in testing the tensile strength of test specimens cut from lap-soldered thin sheets.

In certain cases, due to non-coincidence of the axes of symmetry in the lap-soldered halves of the test specimen, during testing, the seam area is liable to be placed at a certain angle with the direction of the tensile stresses, thus leading besides tensile stresses, to bending stresses, more difficult to be ascertained (Figure 144). Shear strength values, determined according to the load, divided by lap area of the seam, do not reflect the true and intricate process of destruction of the soldered joint. Bending stresses do not appear in such tests if double lap-soldered test specimens are used (Figure 145).

A special method for testing rupture strength of soldered joint has been devised by Chadwick. Figure 146 shows a diagrammatic representation of his test. In this method, the rupture strength is determined by the load

related to the width of the test strip. Figure 147 shows results of testing tin-lead soldered copper sheets, according to this method.

Figure 148 shows a test specimen for testing vibration resistance of soldered joints. Most frequently the specimens involved are of the supported type.

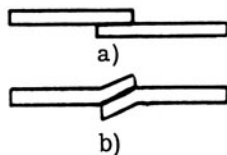


Figure 144. Position of seam area in certain lap-soldered seams during tensile testing:

a—prior to the test; b—after the test.

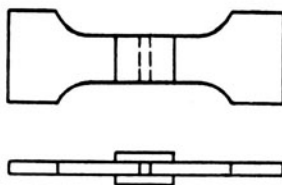


Figure 145. Sketch of a double lap-soldered test specimen for testing shear strength.

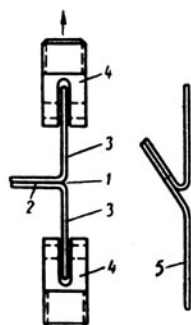


Figure 146. Diagrammatic representation of the Chadwick method for rupture testing of a soldered joint:

1—fillet; 2—soldered seam; 3—soldered tips; 4—clamping vices; 5—shape of test specimen.

Soldered parts working under load are subjected to fracture tests.

So, for instance, the quality of soldered bits of the cutting chain of mining cutters and combines may be judged upon the results of shear testing sintered carbide hard metal tips soldered to the cutting bits /6/. For

this to be done, the cutting bits are rigidly fixed in a special appliance; the hard metal tips project over this appliance, and touch the die of the appliance, the bearing part of which is shaped to suit the projecting lateral side of the tip. Soldering is considered to be satisfactory if the shear strength, as resulted from this testing, does not drop below 10 kg/mm^2 .

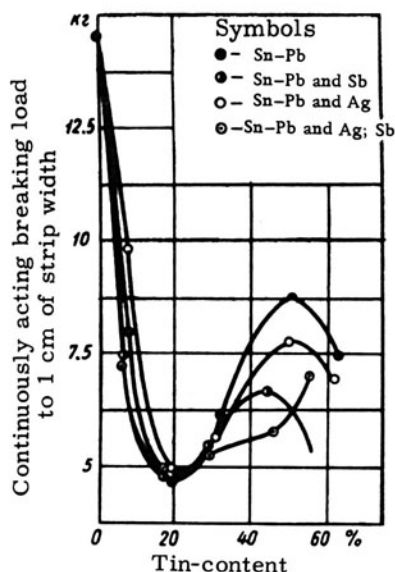


Figure 147. Results of rupture testing of soldered seams on cold-rolled copper sheets 0.46 mm thick, 24 hours after soldering (according to Chadwick)

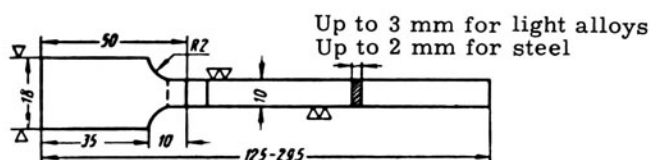


Figure 148. Specimen for testing vibration resistance of lap soldered joints

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